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# THE PHYSICAL METALLURGY OF PRECIPITATION-HARDENABLE STAINLESS STEELS

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THE PHYSICAL METALLURGY OF  
PRECIPITATION-HARDENABLE STAINLESS STEELS

by

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to

OFFICE OF THE DIRECTOR OF DEFENSE  
RESEARCH AND ENGINEERING

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# THE PHYSICAL METALLURGY OF PRECIPITATION-HARDENABLE STAINLESS STEELS

## SUMMARY

The precipitation-hardenable stainless steels have been developed during the past two decades to meet the needs of the defense program. They offer corrosion resistance, fabricability, and strength at room and moderately elevated temperatures. In comparison with titanium and its alloys, they are stronger and can be used at higher temperatures. In many applications the corrosion resistance and fabricability of the precipitation-hardenable stainless steels allow them to compete with the stronger hot-work die steels.

The precipitation-hardenable stainless steels are classified as martensitic (e.g., Stainless W and 17-4 PH), semiaustenitic (e.g., 17-7 PH, PH 15-7 Mo, AM 350, and AM 355), or austenitic (A-286 and HNM). At normal annealing temperatures, these alloys are predominantly austenitic; but, depending on composition and heat treatment, the austenite may transform to martensite on cooling or during mechanical deformation. Classification, therefore, is on the basis of austenite stability.

The martensitic types undergo transformation of austenite to martensite on cooling to room temperature. The transformation results in a partial hardening of the matrix. The martensite which forms is, in most cases, thought to be highly supersaturated with certain solute elements which precipitate in the form of second phases during tempering at temperatures near 900 F. Additional hardening results from this phenomenon.

The composition of the semiaustenitic types is such that after annealing at temperatures near 1950 F they remain austenitic on cooling, being readily fabricable in this form. Subsequent treatment at 1400 F or 1725 F depletes the austenite of chromium and carbon to the extent that martensite forms on cooling to room temperature or -100 F, respectively. Mechanical deformation may also result in transformation. Final hardening is effected during the tempering treatment, as in the case of the martensitic types.

The austenitic precipitation-hardenable stainless steels remain austenitic on cooling to room temperature. A moderate condition of supersaturation is developed during cooling as a result of the decreasing solubility of solute elements with decreasing temperature. Precipitates form at temperatures near 1300 F, which strengthen the austenitic matrix.

Factors to be considered in the fabrication and heat treatment of these alloys include the following:

- (1) Mechanical properties are critically dependent on proper heat treatment.
  - (2) Mechanical deformation may have a bearing on response to certain thermal treatments.
  - (3) Dimensional changes occur during heat treatment.
  - (4) After certain heat treatments these alloys are subject to intergranular attack in acid solutions.
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## INTRODUCTION

Stainless steels were patented in the United States,<sup>(1)</sup> Canada,<sup>(1)</sup> Great Britain,<sup>(2)</sup> Germany,<sup>(2,3)</sup> and France<sup>(1)</sup> during the second decade of the present century. The three classes of stainless steels developed during that period, the martensitic, ferritic, and austenitic classes, still constitute the bulk of the world's stainless steel production. Of course, important improvements have been made through the years. The constitution and general metallurgy of these steels, as well as the technology of their production, continues to be the subject of numerous technical papers.

During World War II, the need for stronger corrosion-resistant materials spurred the development of the first precipitation-hardenable stainless steel, a martensitic grade designated Stainless W. Information on this development was released in 1946 by the Carnegie Illinois Steel Company.<sup>(4)</sup> In 1948 another martensitic precipitation-hardenable stainless steel, 17-4 PH, was introduced by Armco Steel Corporation.

Austenitic precipitation-hardenable stainless steels were introduced soon after the martensitic grades. Allegheny Ludlum Steel Corporation began marketing A-286 in 1951, while Crucible Steel Company of America developed HNM during the Korean conflict.

Another development in the field of stainless steel metallurgy was the evolution of the semiaustenitic alloys. These stainless grades are austenitic in the annealed condition, but can be made martensitic by appropriate thermal treatment. In 1948, Armco introduced 17-7 PH and a double-aging technique for hardening the alloy. Allegheny Ludlum introduced AM 350 in 1954, along with a subzero hardening treatment. Newer modifications of these steels were introduced later, AM 355 in 1955 and PH 15-7 Mo in 1957. All four alloys can be hardened by either of the techniques mentioned.

Armco's 17-7 PH and PH 15-7 Mo are presently considered to be true precipitation-hardenable alloys. These alloys are initially hardened when austenite is forced to transform to martensite. Additional strengthening occurs during an aging treatment, when hardening phases precipitate within the martensite. AM 350 and AM 355, on the other hand, are hardened principally by the austenite-to-martensite transformation. Some additional strengthening of these two alloys results from tempering the martensite. The mechanical and thermal treatments which result in martensite formation are very similar for both groups of alloys. The aging treatments prescribed for the Armco alloys are very similar to the tempering treatments applied to the Allegheny alloys. In addition, the mechanical properties which result from these like treatments are of the same order. Because of these similarities, AM 350 and AM 355 are often included with 17-7 PH and PH 15-7 Mo as semiaustenitic precipitation-hardenable stainless steels.

In recent years the need for high-strength, heat-resistant and corrosion-resistant materials with good fabricability and weldability has been emphasized by the defense program of the United States. The precipitation-hardenable stainless steels have helped to meet that need. The martensitic precipitation-hardenable stainless steels offer yield strengths in the order of 180,000 psi and retain a usable portion of their strength at temperatures up to 900 F. The semiaustenitic precipitation-hardenable stainless steels offer ease of fabrication, yield strengths in the order of 200,000 psi, and good retention of strength at temperatures up to about 900 F. Materials in both of these groups can be welded by ordinary methods and possess very good corrosion resistance. In addition, they can be used at temperatures higher than those which limit the use of titanium alloys, 500 F to 600 F. Also their strength, but not their strength-to-weight ratio, is superior to that of the titanium alloys over their entire range of application. For applications requiring exposure to temperatures in the range 800 F to 1300 F the austenitic precipitation-hardenable stainless steels offer yield strengths in the order of 100,000 psi. The stainless steels rival the hot-work die steels for applications requiring exposure to temperatures up to 1000 F. While the stainless steels offer slightly less strength, they are easier to fabricate and have better corrosion resistance. Applications at temperatures above 1300 F call for the use of the so-called superalloys.

The physical metallurgy of the conventional stainless steels, while complex, is fairly well understood. The use of the precipitation mechanism to harden stainless steels, however, is a comparatively recent addition to metallurgical technology. Published information on the physical metallurgy of precipitation-hardenable stainless steels is still rather scarce, though there are some publications on the subject(5,6).

The objective of this report is to summarize present knowledge of the physical metallurgy of precipitation-hardenable stainless steels. In addition, the manner in which the hardening mechanisms govern heat treatment and fabrication is discussed. Approximate mechanical properties are presented only for illustrative purposes. The physical and mechanical properties of precipitation-hardenable stainless steels have been compiled in a companion report(7).

It must be pointed out here that the explanations presented for certain phenomena observed in some of these steels, particularly those relating to strengthening by aging or tempering, must be considered as hypothetical at present. Although these hypotheses are generally accepted, additional critical experiments are required fully to substantiate them.

The text is divided into four major sections. The first section, entitled "The Physical Metallurgy of Stainless Steels", is a review of the classification of stainless steels and those metallurgical phenomena which are common to most or all of the materials subsequently considered. In this section the emphasis is placed on the explanation of basic mechanisms.



While a thorough review of these subjects is beyond the scope of this report, references to complete works are given.

The remaining three sections treat separately the three classes of precipitation-hardenable stainless steels:

- (1) The martensitic types (Stainless W and 17-4 PH)
- (2) The semiaustenitic types (17-7 PH, PH 15-7 Mo, AM 350 and AM 355)
- (3) The austenitic types (A-286 and HNM).

Each of these sections deals with heat treatment and fabrication. The emphasis in these sections is on the application of basic metallurgical principles to these operations.

## THE PHYSICAL METALLURGY OF STAINLESS STEELS

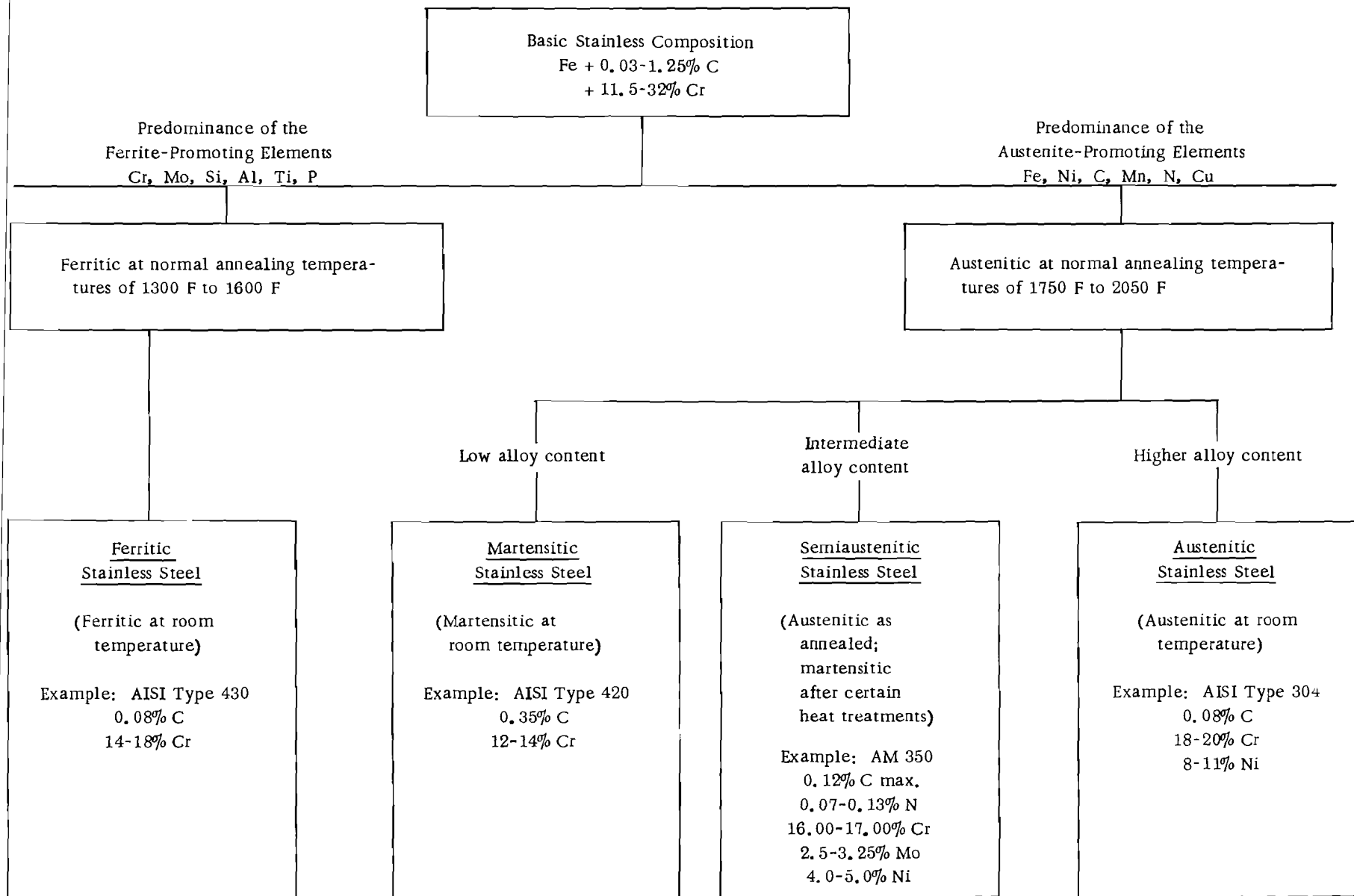
The stainless steels are essentially alloys of iron, carbon, and chromium; but they may also contain significant amounts of other alloying elements. The iron-carbon system forms the base for the stainless steels and provides them with the wide range of mechanical properties and the versatility characteristic of this system. Carbon is used in amounts up to 1.25 per cent. Chromium, which is used in amounts ranging from 11.5 to 32 per cent, accounts for the remarkable corrosion and oxidation resistance of this series of alloys. In addition, chromium retards the rate at which some transformations take place. Both chromium and carbon play important roles in heat treatment and therefore contribute largely to the mechanical properties obtained.

Nickel may be present in stainless steels in almost any amount. A major function of this element is to promote the presence of austenite. This is discussed in greater detail in the next section. In addition, nickel enhances resistance to corrosion.

Many other elements may be found in stainless steels. Manganese and silicon appear to serve the same purpose as they do in carbon steels, combining with sulfur and oxygen, respectively. Manganese and nitrogen may also be substituted for nickel to promote the austenitic structure in stainless steels. Molybdenum is used to increase elevated-temperature strength and to improve resistance to attack by halide solutions. Titanium, columbium, and tantalum are added to some stainless grades to prevent the formation of chromium carbides during certain thermal treatments. The elements aluminum, copper, and titanium are believed to produce precipitation-hardening characteristics.

### Classification by Composition

Stainless steels are commonly classified by their room-temperature constitution, i.e., the crystallographic structure of the matrix at room temperature<sup>(8)</sup>. The constitution of stainless steels at this temperature is determined both by composition and by heat treatment. Their classification into four groups, the ferritic, martensitic, semiaustenitic, and austenitic stainless steels, on the basis of their room-temperature constitution is approached here from the point of view of composition. Each element in a stainless steel plays a dual role. The function of certain elements in promoting the formation or retention of either ferrite or austenite at elevated temperatures is discussed first. Their other function, that of controlling phase transformation on cooling, is discussed thereafter. The classification of stainless steels, on the basis of their composition, is outlined in Figure 1.



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FIGURE 1. CLASSIFICATION OF STAINLESS STEELS BY COMPOSITION

It is seen from Figure 1 that the elements present in stainless steels may be divided into two groups, ferrite promoters and austenite promoters. Ferrite promoters are those elements which, when added to the steel, encourage the presence of ferrite at normal annealing temperatures. Austenite promoters are those elements which favor the formation of austenite at normal annealing temperatures. Whether a given stainless steel will be austenitic or ferritic at an elevated temperature depends on the relative proportions of the elements present from these two groups, as well as on the details of the annealing treatment.

Chromium, molybdenum, silicon, titanium, aluminum, and phosphorus are ferrite promoters. When these elements are present in sufficient quantity to overbalance the austenite promoters, ferrite develops at normal annealing temperatures. Nitrogen, carbon, nickel, manganese, and copper, as well as iron, are austenite promoters. When these elements outweigh the ferrite promoters, austenite is present at normal annealing temperatures.

Figure 2 is a highly idealized pictorial aid illustrating the combined effects of composition and temperature on the phases present at elevated temperatures.

Several formulae which attempt to relate the phase present at normal annealing temperatures to the relative proportions of the austenite-promoting elements and ferrite-promoting elements have been published. While these formulae were usually derived for weld metal or cast structures rather than for wrought forms, they illustrate the effects of several elements on compositional balance. Schaeffler<sup>(9)</sup> has presented the following formula for the minimum amounts of nickel, manganese, and carbon required to assure that weld deposits will be entirely austenitic and will contain no ferrite:

$$\text{Ni}^* + 1/2 \text{ Mn} + 30 \text{ C} = \frac{(\text{Cr} + 1.8 \text{ Mo} + 2.5 \text{ Si} + 2 \text{ Cb} - 16)^2}{12} + 12.$$

Other studies have been made by Post and Eberly<sup>(10)</sup> and by Gow and Harder<sup>(11)</sup>. Kinzel and Crafts<sup>(12)</sup> have published a volume dealing with phase stability as well as other aspects of stainless steel metallurgy.

Stainless steels which contain a predominance of the ferrite-promoting elements are usually annealed in the range 1300 F to 1600 F. This treatment results in an essentially ferritic matrix. Heating to higher temperatures, as might be encountered in hot-working operations, allows some austenite to form in the matrix. The tendency of austenite to form as temperature is increased above 1600 F is reduced by larger additions of the ferrite promoter, chromium<sup>(13)</sup> (see Figure 2).

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\*Chemical symbols represent weight per cent.

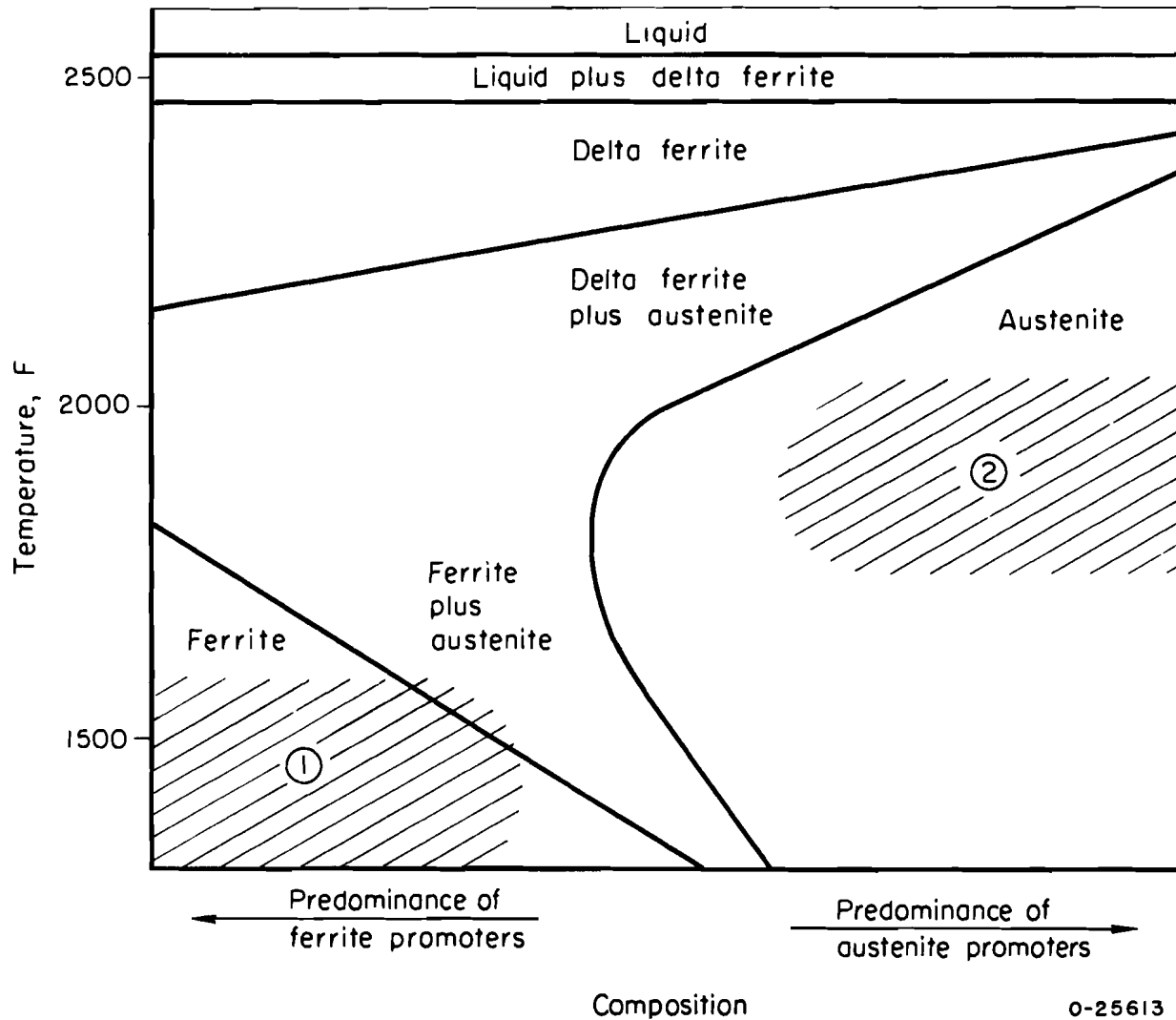


FIGURE 2. ELEVATED-TEMPERATURE CONSTITUTION OF STAINLESS STEELS

Cross hatched areas represent those ranges of composition and temperature normally used to obtain (1) ferrite or (2) austenite.

Stainless steels which contain a predominance of the austenite-promoting elements are normally annealed in the range 1750 F to 2050 F. This treatment usually results in a matrix which is entirely austenitic. Some ferrite may form if these materials are heated to temperatures above the normal annealing range. This ferrite, which forms in austenitic matrixes at very high temperatures, i.e., slightly below the melting range, is termed delta ferrite to distinguish it from the ferrite which forms at lower temperatures. The tendency for delta ferrite to form at very high temperatures is reduced by larger amounts of the austenite-promoting additions (see Figure 2).

The preceding paragraphs have contained a discussion of how composition and heat treatment determine the structure of stainless steels at elevated temperatures. The transformations which may occur on cooling, and how they are governed by composition, are discussed in the succeeding paragraphs. Examples of each of the four classes of stainless steels, as based on their structure at room temperatures, are presented.

The stainless steels that are balanced so as to be ferritic in the range 1300 F to 1600 F do not transform on cooling from temperatures in this range; they remain ferritic at room temperature regardless of cooling rate. On the basis of their structure at room temperature they are classed as ferritic stainless steels. AISI Type 430, with 14 to 18 per cent chromium, and about 0.08 per cent carbon, is an example of a ferritic stainless steel.

As is the case with the hardenable plain-carbon and low-alloy steels, the austenitic stainless steels may undergo transformation from austenite to martensite on cooling below some temperature characteristic of the material. The temperature at which the first traces of martensite appear is termed the  $M_s$  temperature. In stainless steels,  $M_s$  may be as high as 600 F, in which case transformation occurs on cooling to room temperature. This characteristic temperature may also be so low that no transformation will occur even when the steel is cooled to liquid-nitrogen temperature, -320 F.

The  $M_s$  temperature depends primarily on the chemical composition of the austenite, although such factors as grain size and annealing temperature are also important. Most elements, when dissolved in austenite, lower the  $M_s$  temperature. Only aluminum and cobalt are known to raise  $M_s$ . At least two empirical equations relating the  $M_s$  of stainless steels to austenite composition have been published:

$$M_s(F) = 75(14.6 - \%Cr) + 110(8.9 - \%Ni) + 3000 [0.068 - \%(C + N)] + 60(1.33 + \%Mn) + 50(0.47 - \%Si). \quad (\text{Ref. 14})$$

$$M_s(F) = 2160 - 66(\%Cr) - 102(\%Ni) - 2620(\%C + N). \quad (\text{Ref. 15})$$

These formulae indicate that the  $M_s$  temperature is decreased as alloy content is increased. Figure 3 illustrates this.

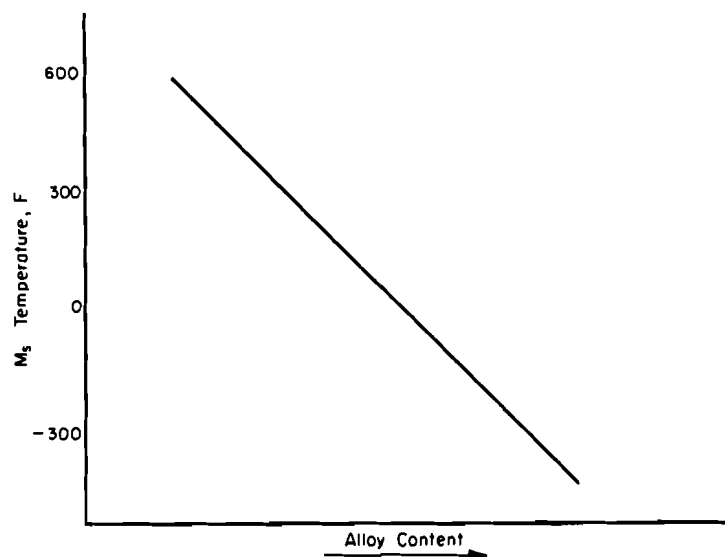


FIGURE 3. THE EFFECT OF ALLOY CONTENT ON  $M_s$  TEMPERATURE

Chromium, molybdenum, and silicon may play a dual role in their effect on austenite. These elements discourage the formation of austenite at elevated temperatures and are therefore classed as ferrite promoters. Yet if austenite is formed in spite of their presence, chromium, molybdenum, and silicon favor retention of the austenite on cooling. Thus these elements, together with all of the austenite-promoting elements, are known as austenite stabilizers. It is essential to distinguish between the elevated-temperature function of certain elements in promoting the formation of either austenite or ferrite and their low-temperature function of stabilizing austenite against transformation to martensite.

Stainless steels which are austenitic at normal annealing temperatures and are of high alloy content have  $M_s$  temperatures well below room temperature. These materials are known as austenitic stainless steels because austenite is retained on cooling to room temperature. Nickel is a usual alloying element in austenitic stainless steels because it not only promotes the formation of austenite, but also reduces its  $M_s$  temperature. Manganese and nitrogen are also used for these purposes. A typical example of an austenitic stainless steel is AISI Type 304, which contains 18 to 20 per cent chromium, 8 to 11 per cent nickel, and a maximum of 0.08 per cent carbon.

Some stainless steels are austenitic at elevated temperatures but, because they contain smaller amounts of alloying additions, may transform

to martensite upon cooling to room temperature. These are known as martensitic stainless steels. A typical example is AISI Type 420, which contains 12 to 14 per cent chromium and about 0.25 to 0.35 per cent carbon.

By careful control of composition and heat treatment, stainless steels which are of intermediate austenite stability can be produced. The semi-austenitic stainless steels, as they are called, are austenitic upon cooling from annealing temperatures to room temperature. In this condition they are soft and ductile and therefore are amenable to fabricating operations. Subsequent treatment at a temperature between 1200 F and 1750 F allows some of the carbon dissolved in the austenite to precipitate in the form of chromium carbides. The depletion of chromium and carbon from the austenite reduces its stability; i.e., raises  $M_s$ . Upon cooling to room temperature or below, the austenite-to-martensite transformation reaches completion. The temperature at which transformation is complete depends largely on the extent of carbon depletion. AM 350 is an example of a semi-austenitic stainless steel. This alloy contains 16.00 to 17.00 per cent chromium, 2.5 to 3.25 per cent molybdenum, 4.0 to 5.0 per cent nickel, and about 0.10 per cent each of carbon and nitrogen.

Precipitation-hardenable stainless steel alloys have been developed by making certain alloying additions to martensitic, semiaustenitic, and austenitic base alloys. Thus, there are martensitic stainless steels which are similar to, but distinct from, martensitic precipitation-hardenable stainless steels. Likewise, there are both austenitic stainless steels and austenitic precipitation-hardenable stainless steels. All of the semi-austenitic stainless steels are either precipitation hardenable or classed as such. Some ferritic stainless steels are inherently precipitation hardenable, but none have been specifically developed to exploit this characteristic.

In the cases of some of the alloys discussed in this report, it has yet to be demonstrated that hardening is attributable to the precipitation of second phases. Considerable research will be required to determine whether precipitation hardening or another mechanism is responsible for the hardening of these alloys. At present, however, the observed hardening effects are best explained on the basis of the precipitation-hardening mechanism.

### Austenite Conditioning

The precipitation of chromium carbides in semiaustenitic stainless steels for the purpose of raising the  $M_s$  temperature is termed austenite conditioning. The precipitation is usually accomplished by heat treating in the range 1200 F to 1750 F. "Aging" is a term often applied to austenite conditioning treatments at lower temperatures in this range, e.g., 1400 F; while a treatment near 1700 F is sometimes called a "trigger anneal".

The amount of carbon which can be dissolved in austenite is a function of temperature and composition(16,17,18). Greater amounts of carbon are soluble at higher temperatures, as illustrated by Figure 4. About 0.02 to 0.03 per cent carbon is soluble at 1400 F, while about 0.30 per cent carbon



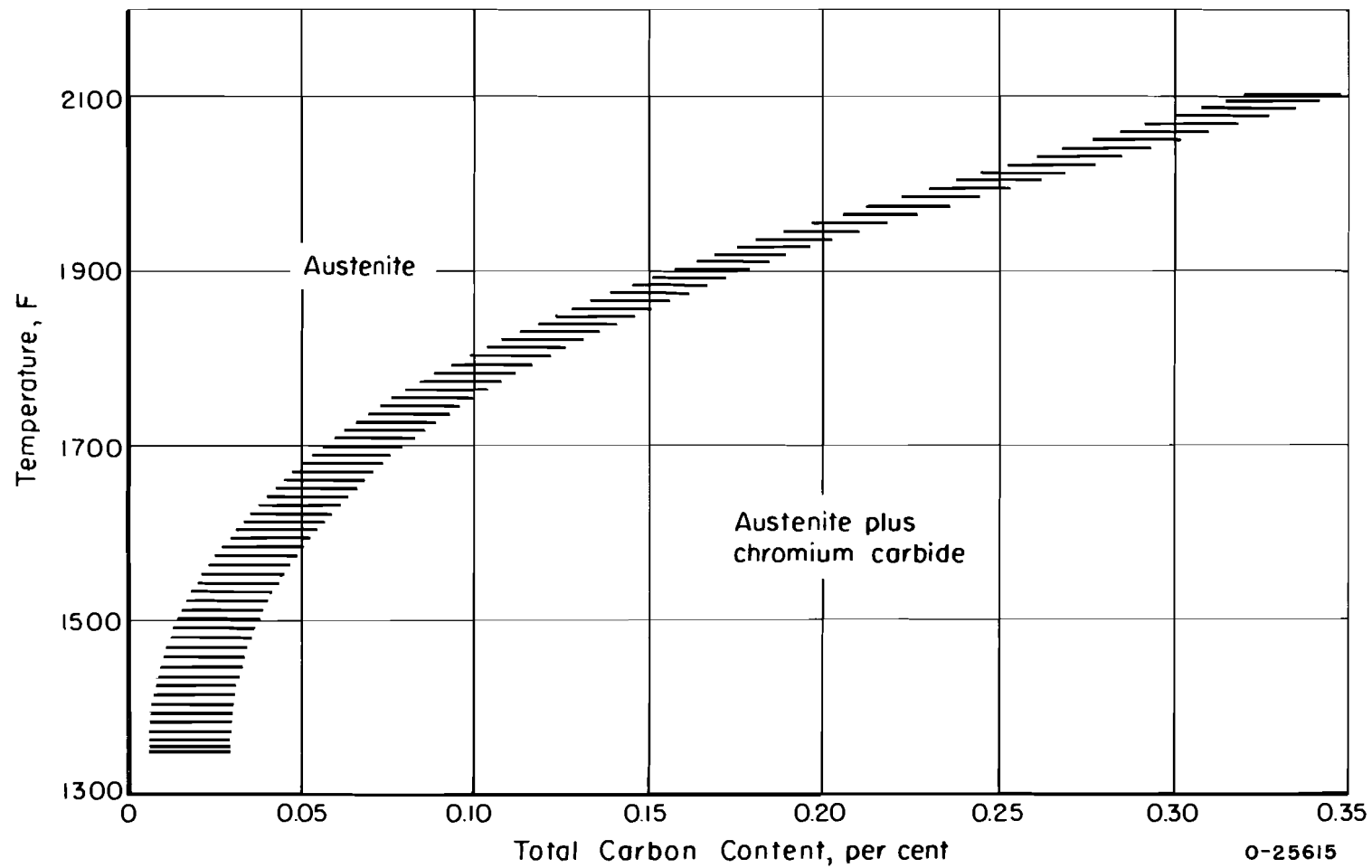


FIGURE 4. THE SOLUBILITY OF CARBON IN AUSTENITE

is soluble in austenite at 2100 F. The elements columbium, titanium, and tantalum, because of their high affinity for carbon, sharply reduce the solubility of carbon in austenite over a wide temperature range. These elements, however, are not purposely added to semiaustenitic stainless steels.

The semiaustenitic stainless steels are usually solution annealed at about 1950 F. This treatment, as the name implies, allows all of the carbon to be dissolved in the austenite. The composition of these alloys is such that when all of the carbon is in solution, the  $M_s$  temperature is well below room temperature. Thus, solution-annealed material may be subjected to subzero temperatures, as may be encountered during winter shipment or storage, without danger of transformation.

Subsequent to solution annealing and fabrication, the semiaustenitic stainless steels are usually given an austenite-conditioning treatment. During this treatment, chromium carbides are precipitated from the austenite, since only a portion of the total carbon content is soluble at the austenite-conditioning temperature. The depletion of dissolved chromium and carbon raises the  $M_s$  temperature of the austenite. The semiaustenitic stainless steels are usually balanced such that a "trigger anneal" at about 1725 F reduces the carbon content of the austenite by an amount great enough to raise the  $M_s$  to the vicinity of room temperature. Subsequent cooling to -100 F is employed to transform the austenite to martensite. "Aging" at about 1400 F reduces the carbon content of the austenite to a greater extent than does treatment at 1725 F. The 1400 F austenite-conditioning treatment usually raises the  $M_s$  to such a temperature that transformation is essentially complete on cooling to room temperature.

During austenite conditioning, chromium carbide particles precipitate at sites of high internal energy. Grain boundaries, phase boundaries, and slip planes constitute such sites. In solution-annealed material, austenite conditioning precipitates chromium carbides at grain boundaries and phase boundaries. In solution-annealed and cold-worked material, carbides precipitate at the slip planes as well as at grain boundaries and phase boundaries.

The formation of chromium carbides depletes austenite of chromium as well as carbon. If carbides are formed at the grain boundaries, there must exist a region of chromium-impoverished austenite adjacent to the grain boundaries. Since corrosion resistance is strongly dependent on chromium content, chromium impoverishment leads to poorer corrosion resistance. In particular, the existence of a continuous grain boundary network of chromium-impoverished austenite in proximity with the more highly corrosion-resistant grains provides the necessary conditions for rapid electrochemical attack in the presence of ionic solutions. Material that is less corrosion resistant as a result of austenite conditioning is said to be "sensitized". Cold work, either before or after austenite conditioning, reduces the continuity of the chromium-impoverished network and therefore combats sensitization.

### The Martensite Reaction

Steels which are austenitic at elevated temperatures may undergo a solid-state transformation on cooling or they may remain austenitic. Transformation, if it occurs, can take place in two ways. If conditions are such that rapid diffusion can occur, the transformation can proceed by nucleation and growth. Otherwise, the transformation can proceed by the martensite reaction. It is not uncommon to have transformation occurring in both ways in some steels during cooling: first by nucleation and growth and then, at lower temperatures, by the martensite reaction. Transformation of carbon and alloy steels by nucleation and growth can occur over a range of temperatures and result in diverse products. In the stainless steels, however, transformations of this type are more limited. The precipitation of chromium carbide from austenite, as described in the preceding section, occurs by nucleation and growth. This reaction is not considered a transformation because no phase change occurs. However, the austenitic matrix is depleted in carbon and may transform to ferrite in some martensitic grades on prolonged holding at temperatures near 1200 F. Ferrite does not form isothermally from carbon-depleted austenite in the austenitic or semiaustenitic stainless steels.

Nucleation-and-growth transformations can be suppressed by rapid cooling because they are diffusion-controlled reactions. Rapid cooling restricts the time available for a suitable nucleus to form by diffusion of atoms. At room temperature, diffusion rates are negligible. If the precipitation of carbides followed by transformation of austenite to ferrite is prevented by rapid cooling, the transformation of austenite to martensite may occur as temperature is reduced. Whether or not austenite will transform to martensite depends primarily on composition and temperature, as discussed in a previous section.

Figure 5 is a generalized time-temperature-transformation curve for martensitic stainless steels. Rapid cooling (1) results in martensite. Isothermal holding at temperatures near 1200 F for a limited time followed by cooling (2) results in ferrite, carbide, and martensite, the remaining austenite having transformed to martensite on cooling. Prolonged isothermal holding near 1200 F followed by cooling (3) results in ferrite plus carbide.

The martensite reaction has the following characteristics:

- (1) The reaction proceeds primarily during cooling between two temperatures,  $M_s$  and  $M_f$ , but martensite may also form during isothermal holding between these temperatures.
- (2) The reaction is not suppressible by rapid cooling.

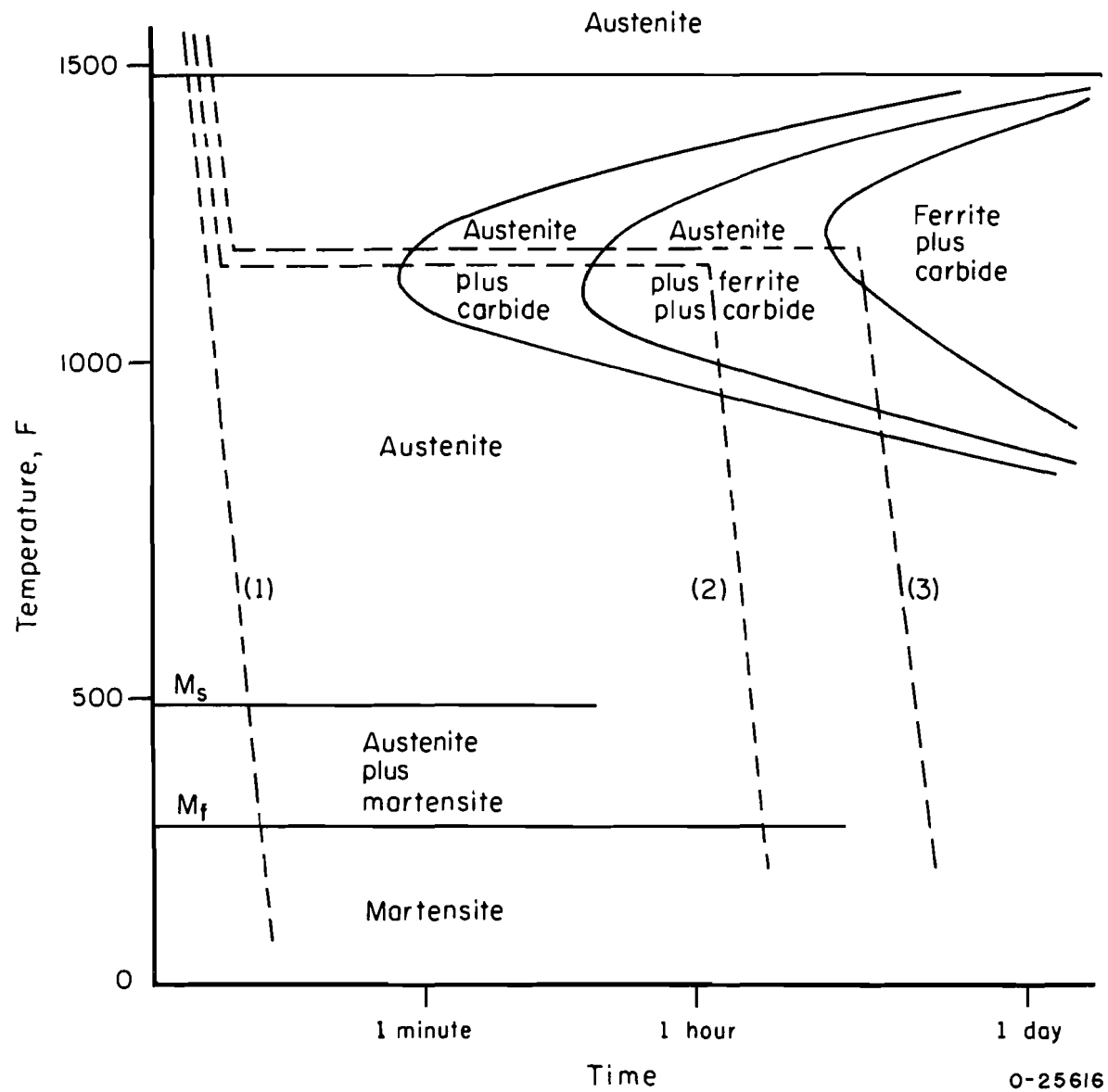


FIGURE 5. TIME-TEMPERATURE-TRANSFORMATION OF MARTENSITIC STAINLESS STEELS

- (3) The reaction is diffusionless or isoconcentrational; the martensite formed is of the same composition as the parent austenite.
- (4) The reaction proceeds by the rapid formation of individual full-size plates of martensite rather than by the growth of previously formed plates.
- (5) Cessation of cooling during the reaction, or very slow cooling, may result in a reduced tendency of austenite to transform to martensite on subsequent cooling, a condition known as austenite stabilization.
- (6) Deformation at temperatures up to about 300 F above the  $M_s$  induces transformation of austenite to martensite.
- (7) The transformation is characterized by considerable hysteresis, martensite reverting to austenite only at temperatures considerably above the  $M_s$ .
- (8) The body-centered tetragonal lattice of the martensite forms with a definite crystallographic relation to the face-centered cubic lattice of the parent austenite.
- (9) In stainless steels an expansion of about 0.4 per cent accompanies the formation of martensite; a contraction of the same amount occurs when martensite reverts to austenite on heating.

Two theories to explain the characteristics of the martensite reaction have been advanced. One of these, proposed by Cohen, Machlin, and Paranjpe<sup>(19)</sup>, and extended by Machlin and Cohen<sup>(20)</sup>, postulates the existence of strained regions which act as martensite nuclei. These strain embryos have been identified with screw-type dislocations. On cooling, the thermodynamic conditions favoring transformation are developed. The most highly strained regions become nuclei at the  $M_s$ . On continued cooling, regions of lower strain become activated. When a nucleus forms it grows with nearly the speed of sound by a shear mechanism. There is a coordinated movement of atoms, over a fraction of an interatomic distance, to form a new lattice. Nucleation and shear continue during cooling until the  $M_f$  temperature is reached and the structure is wholly transformed.

The preceding paragraph describes athermal transformation, that which occurs only on continued cooling. The transformation, however, has been observed to take place on isothermal holding between the  $M_s$  and  $M_f$  temperatures. Embryos with energies just under that necessary for nucleation at a given holding temperature may become activated during the holding time when the energy of thermal vibration is superimposed upon the

strain energy. The isothermal reaction does not result in complete transformation.

Mechanical deformation results in the formation of strained regions. These regions can nucleate the martensite reaction. The formation of martensite itself also strains the lattice, making the reaction somewhat autocatalytic. During isothermal holding, those strain embryos which do not become activated may undergo relaxation. The relaxation lowers the energy available for nucleation and results in stabilization.

Another theory, proposed by Fisher, Holloman, and Turnbull<sup>(21)</sup>, postulates the existence of carbon-poor regions in the austenite which can nucleate the transformation to martensite. On cooling, the largest of these regions are the first to become martensite nuclei when the proper thermodynamic conditions are developed. If cooling is continued below the  $M_s$ , smaller carbon-poor regions become activated. Martensite plates form rapidly by consecutive transfer of atoms over a fraction of an interatomic distance from the austenitic matrix to the growing martensite plate.

The higher the temperature at which austenite is formed during annealing, the lower will be the  $M_s$  temperature. Higher austenitizing temperatures result in greater solution of carbon, an element which reduces  $M_s$  when dissolved in austenite. But even after all the carbon has been taken into solution further increases in austenitizing temperature still reduce  $M_s$ . This is because the distribution of carbon in the austenite becomes more homogeneous as temperature is increased, or the size and number of carbon-poor regions are reduced. Alternatively, strained regions are reduced in number and energy, as austenitizing temperature is increased.

During the transformation from face-centered cubic austenite to body-centered tetragonal martensite all alloying constituents are retained in solution. Carbon atoms take up positions at the edge centers of the unit cells. Since these positions are not quite large enough to accommodate the carbon atoms, the unit cell is strained from a cubic to a tetragonal configuration. These strains, which increase with carbon content, account for the high strength of martensite.

Freshly formed martensite is brittle as well as strong. This brittleness limits its usefulness. Martensitic structures are usually tempered in the range 300 F to 1100 F. During this heat treatment the high internal stresses are relieved. This stress relief is accompanied by a reduction in brittleness and, at higher tempering temperatures, a reduction in strength. At the lower tempering temperatures, however, the migrating carbon atoms combine with chromium atoms to form minute chromium carbides which counteract softening.

The martensite reaction has been thoroughly reviewed by Cohen<sup>(22)</sup>, by Greninger and Troiano<sup>(23)</sup>, and by Bilby and Christian<sup>(24)</sup>.

### Precipitation Hardening

The means of strengthening alloys by quenching from an elevated temperature and aging at a lower temperature has been known for almost a half century. Duralumin, basically aluminum plus 4.5 per cent copper, was the first commercial precipitation-hardening alloy; others have since been developed. During the past two decades, precipitation-hardening stainless steels have been developed and placed on the market.

Early investigators realized that the solubility of copper in aluminum is higher at elevated temperatures than at room temperature. They postulated, therefore, that quenching Duralumin from elevated temperatures results in a supersaturated solution of copper in aluminum at lower temperatures. They also believed that the condition of supersaturation could be relieved by precipitation of  $\text{CuAl}_2$  during isothermal holding at some moderate temperature, a treatment termed aging. The strengthening effect of aging was originally thought to be due to a keying action of the precipitate particles, making slip along crystallographic planes more difficult.

As more information was made available it became necessary to modify the keying theory of precipitation hardening. It was discovered that considerable hardening, and frequently maximum hardening, can take place during aging before any precipitate is observed or before any change in lattice dimensions can be measured. The keying theory could not account for this. Neither could the keying theory account for the increase in resistivity which occurs during aging. The coherency theory of precipitation hardening was developed to account for these observations.

The coherency theory of precipitation hardening is concerned mainly with the way in which precipitates are formed during the aging treatment. When conditions are such that precipitation can occur, the reaction begins with the segregation of solute atoms to particular crystallographic planes. Thin plates of the solute atoms form. The lattice of the precipitate particle is originally coherent with the lattice of the matrix; that is to say that there is crystallographic conformity between the two lattices. The enforced registry between two lattices of somewhat different spacing leads to severe strains. These coherency strains account for the hardening effect of the precipitation reaction.

Continued holding in the precipitation range of temperatures allows the precipitate particles to grow. When the coherency strains, which increase in magnitude with precipitate size, reach a critical value shearing occurs along the plane of conformity. Then, both the precipitate and the matrix assume their stable lattice dimensions. The release of the coherency strains results in a local hardness reduction. When this condition becomes general the structure is said to be overaged.

The coherency theory of precipitation hardening is consistent with the observation that considerable hardening occurs before precipitates become visible in the microstructure. Only the incoherent particles can be seen under the microscope. Coherent particles cannot be seen, because of their small size and atomic registry with the matrix. The coherent precipitates interfere with the flow of electrons and thus increase electrical resistivity.

The first step in precipitation hardening is the solution heat treatment. In the case of precipitation-hardenable stainless steels this treatment consists of a short soak in the range 1650 F to 2050 F, the exact treatment depending on the composition and the properties desired. The purpose of this treatment is to take into solution the elements which eventually form hardening precipitates. The solution heat treatment may also serve as an anneal or as an austenite conditioning treatment (as previously discussed) in stainless steels.

The second step in precipitation hardening is the development of a condition of supersaturation. Since most alloying elements are much more soluble at the solution annealing temperature than at room temperature, supersaturation of solute elements may be achieved by quenching. Quenching, or at least rapid cooling, prevents precipitation of solute elements during cooling by limiting the time during which precipitate embryos can grow to stable nuclei by the process of diffusion. At room temperature, diffusion in stainless steels is so slow that precipitation does not occur.

Many alloying elements are much less soluble in martensite than in austenite. For this reason the degree of supersaturation developed on quenching can be extended by forcing austenite to transform to martensite. The elements which remain in solution during quenching also remain in solution during the martensite transformation. This transformation is often forced by subzero cooling; or the transformation may occur, after an appropriate austenite conditioning treatment, on cooling to room temperature. Cooling through the martensite transformation range of temperatures must not be so slow as to allow stabilization of austenite.

Treatment of the alloy for a period of time at a selected intermediate temperature constitutes the third step in the precipitation-hardening process, i.e., the aging treatment. This treatment represents a compromise between thermodynamic and kinetic variables. The high degree of supersaturation existing in the alloy (either austenitic or martensitic) at room temperature provides a strong driving force for precipitation. The negligible rate of diffusion in stainless steels at this temperature, however, prevents the formation of precipitates. At somewhat higher temperatures the diffusion rate is great enough to allow the atom migrations which lead to the formation of precipitates. While the diffusion rate (kinetic variable) increases with temperature, the degree of supersaturation (thermodynamic variable) decreases with temperature. At some temperature the martensite begins to revert to austenite, relieving the condition of supersaturation.



The increased solubility of the critical alloying elements as temperature is increased may also relieve supersaturation. When this occurs, no precipitation can take place even though the rate of diffusion may be great. Thus, two temperature-dependent factors, the degree of supersaturation and the rate of diffusion, combine to produce a maximum amount of precipitate in a given period of time at some intermediate temperature.

The precipitation of second phases during aging results in a slight physical contraction. If the aging process is limited to the formation of coherent precipitates, the contraction is in the order of 0.05 per cent. If higher temperatures are employed to produce overaging, or reversion of martensite to austenite, the contraction may be several times as great.

The size and distribution of precipitate particles can be controlled, within limits, by varying the duration and temperature of the aging treatment. Lower temperatures produce smaller, but more homogeneously distributed, precipitate particles. These are the most effective strengtheners. Longer holding times are required to form these precipitates, however. At intermediate temperatures the precipitate particles formed are somewhat larger but fewer in number. While these are not as effective in strengthening the structure, the maximum strengthening effect which can be obtained by treatment at this temperature is realized in a shorter time. At temperatures high in the precipitation-hardening range the precipitates grow rapidly and become incoherent. Their hardening effect in this condition is considerably reduced. The effects of the duration and temperature of the aging treatment on hardness are illustrated in Figure 6.

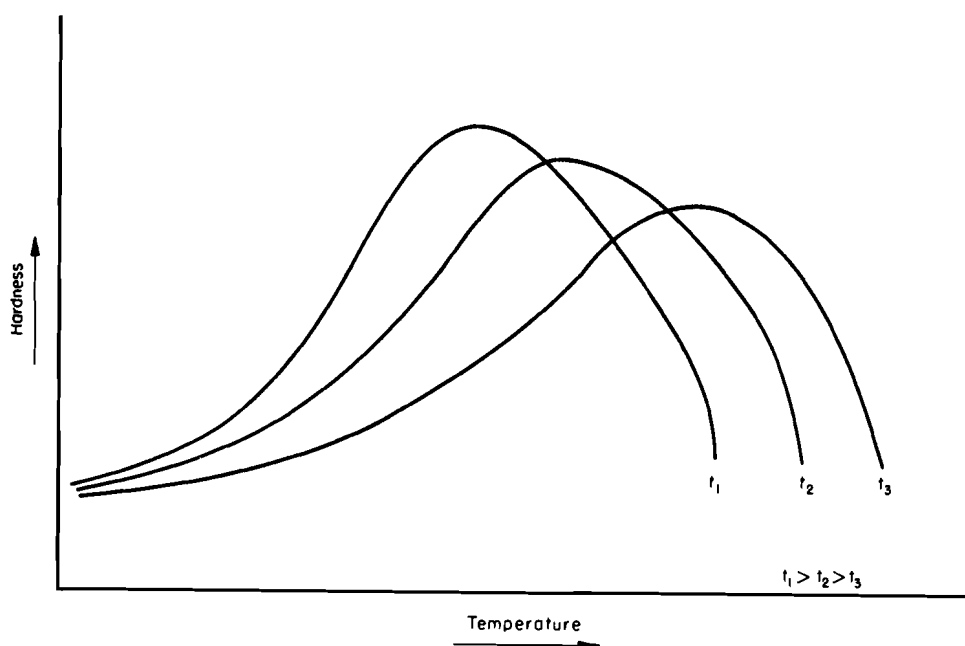


FIGURE 6. THE EFFECTS OF TIME,  $t$ , AND TEMPERATURE OF THE AGING TREATMENT ON HARDNESS

The kinetics of phase changes are discussed by Cottrell<sup>(25)</sup>, while the theory of nucleation and growth has been reviewed by Hardy and Heal<sup>(26)</sup>.

## MARTENSITIC PRECIPITATION-HARDENABLE STAINLESS STEELS

The martensitic stainless steels were the first to which precipitation-hardening additions were made. They were the logical choice, since martensite provides a strong base for further hardening by precipitation. In addition, the transformation from austenite to martensite provides the necessary high degree of supersaturation. Being martensitic at room temperature, however, these steels are not easily formed.

The martensitic precipitation-hardenable stainless steels offer yield strengths in the neighborhood of 180,000 psi and retain a good proportion of their room-temperature strength at temperatures up to 900 F. They are available as bar, wire, plate, extrusions, castings, and forging billets. Sheet and strip forms, although available, are not widely used because of the difficulty encountered in cold working martensitic structures. Finished products are usually machined from bar stock, but castings are also made. The major application of these materials is in the aircraft industry. Blading, bolts, nozzles, pins, landing assemblies, and ribs and stringers, to name a few, are products made from the martensitic precipitation-hardenable stainless steels. Nonmilitary uses include oil-rig valves and boat shafting.

Two steel companies produce martensitic precipitation-hardenable stainless steels. United States Steel Corporation produces Stainless W and Armco Steel Corporation produces 17-4 PH. The chemical compositions of the alloys are presented below.

<u>Element</u>	<u>Stainless W</u>	<u>17-4 PH<sup>(27)</sup></u>
Carbon, %	0.12 max	0.07 max
Manganese, %	1.00 max	1.00 max
Phosphorus, %	0.04 max	0.04 max
Sulfur, %	0.03 max	0.03 max
Silicon, %	1.00 max	1.00 max
Nickel, %	6.0-8.0	3.00-5.00
Chromium, %	16.0-18.0	15.50-17.50
Copper, %	--	3.00-5.00
Aluminum, %	1.0 max	--
Nitrogen, %	0.2 max	--
Titanium, %	1.0 max	--
Columbium plus tantalum, %	--	0.15-0.45
Iron	Balance	Balance

### Stainless W

United States Steel Corporation's Stainless W was placed on the market in 1946. However, because it was not in demand it was not marketed from 1950 to 1957. Stainless W is available again in the form of bar, plate, forging billets, extrusions, wire, sheet, and strip. These forms are available in the solution annealed, overaged, or as-rolled conditions. As solution annealed, and cooled rapidly, the structure of Stainless W is essentially low-carbon martensite. Having a low hardness, about Rockwell C 25, material in this condition can be machined without great difficulty. In the overaged condition, the alloy is more ductile and, therefore, more amenable to mild forming operations. Material can be welded in either the solution-annealed condition or in the overaged condition.

Overaged material must be solution annealed at 1900 F before it can be hardened by aging. Material supplied in the solution-annealed condition can be aged at 950 F directly after fabrication.

A diagram of heat treatments for Stainless W is presented in Figure 7.

### Heat Treatment

Stainless W is solution annealed by holding at  $1900\text{ F} \pm 50\text{ F}$  for a minimum of 15 minutes. During this treatment a portion of the total titanium and carbon content is taken into solution. However, most of the titanium and carbon remains in the form of titanium carbides. These carbides are scattered throughout a matrix of austenite plus about 10 per cent delta ferrite. The titanium in solution is believed to be partly responsible for precipitation hardening during subsequent heat treatment.

Upon cooling from the solution-anneal temperature, Stainless W undergoes transformation from austenite to martensite beginning at about 200 F. The reaction continues during subsequent cooling to room temperature and continues isothermally at room temperature. Some austenite remains untransformed, since the isothermal reaction takes place only very slowly at room temperature. Because the martensite formed is of low carbon content, it is not very strong. Some typical mechanical properties of Stainless W in the solution-annealed condition are presented below.

<u>Property</u>	<u>Stainless W as Solution Annealed</u>
Ultimate Tensile Strength, psi	120,000
0.20 Per Cent Offset Yield Strength, psi	75,000
Elongation, per cent in 2 inches	3-10
Rockwell C Hardness	25

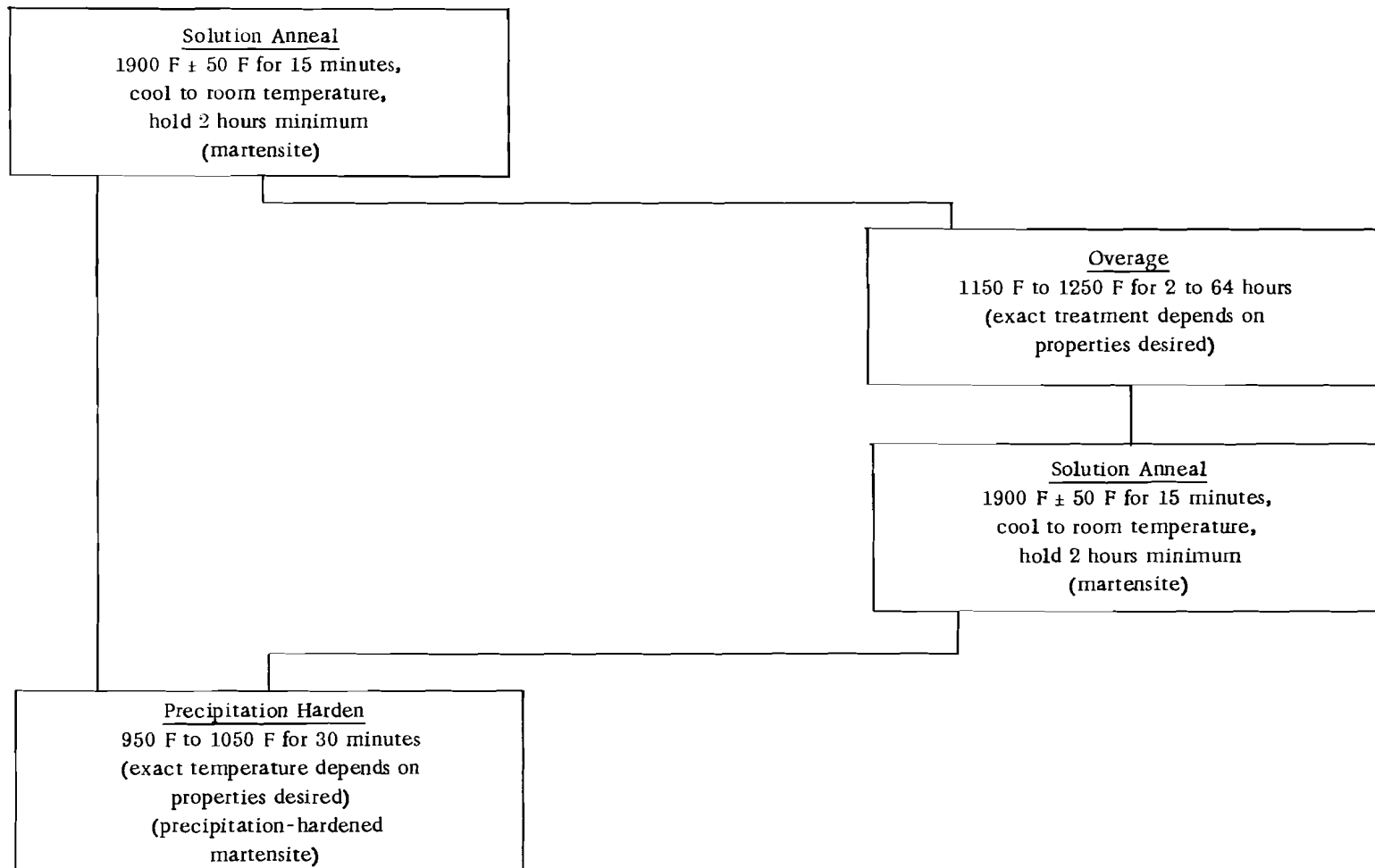


FIGURE 7. THE HEAT TREATMENT OF STAINLESS W

During the transformation of austenite to martensite the titanium, which was soluble at higher temperatures, remains in solution. Because the solubility of this element in martensite is much lower than its solubility in austenite, the martensite which forms is supersaturated with titanium. The martensitic structure is strengthened when a titanium-containing phase is allowed to precipitate within the martensite in a controlled fashion. The recommended aging procedure for Stainless W involves holding the material at 950 F for 30 minutes. Some typical mechanical properties of Stainless W in the precipitation-hardened condition are presented below.

<u>Property</u>	<u>Stainless W as Aged at 950 F for 30 Minutes</u>
Ultimate Tensile Strength, psi	195,000
0.20 Per Cent Offset Yield Strength, psi	180,000
Elongation, per cent in 2 inches	3-10
Rockwell C Hardness	44

The exact nature of the phase or phases precipitating at 950 F is not known. Some recent electron-diffraction studies have indicated that the precipitate may be titanium carbide. Since more hardening is obtained if aluminum is a component of the alloy, it is probable that this element also plays a role in the precipitation reaction.

Mild forming operations are best performed on material overaged by holding at 1150 F to 1250 F for a minimum of 2 hours. During this treatment precipitate particles grow and lose their coherency with the matrix. In addition, martensite reverts to austenite. A considerable amount of this austenite is retained on cooling and imparts improved ductility to the structure. Some typical mechanical properties of Stainless W as overaged at 1150 F are presented below.

<u>Property</u>	<u>Stainless W as Overaged at 1150 F</u>
Ultimate Tensile Strength, psi	134,000
0.20 Per Cent Offset Yield Strength, psi	100,000
Elongation, per cent in 2 inches	20
Rockwell C Hardness	27

Before overaged material can be precipitation hardened it must be given a second solution anneal. This treatment is necessary to redissolve the precipitating phases.

#### The Effects of Variations in Heat Treatment

The recommended solution-annealing treatment for Stainless W is 1900 F  $\pm$  50 F for a minimum of 15 minutes at temperature. At

temperatures higher than 1900 F, greater amounts of titanium carbide are dissolved in the austenite. This has two effects. The higher carbon content of the austenite lowers the temperature range of the martensite transformation, and this results in a greater proportion of retained austenite. The higher titanium content of the martensite which does form, however, allows greater strengthening of this phase on aging. Annealing at temperatures lower than about 1800 F has opposite effects. The two factors controlling strength, the amount of martensite formed and the amount of titanium in the martensite, are affected differently by annealing temperature. These factors, however, combine to produce a maximum in the capacity for hardening after solution annealing in the range 1750 F to 1850 F. The greater amount of retained austenite present after treatment at 1900 F, however, results in greater ductility for material subsequently hardened, with only a slight decrease in strength.

The effects of variations in the duration and temperature of aging treatments have been discussed in a preceding section. For a 30-minute treatment, a temperature of 950 F produces the maximum strengthening effect. Higher aging temperatures result in lower strength but somewhat higher elongation and impact strength. Aging treatments at temperatures somewhat lower than 950 F are capable of producing greater hardening, but only if the duration of the treatment is extended considerably.

Overaging at 1150 F for a minimum of 2 hours produces the greatest elongation. Higher overaging temperatures result in somewhat lower elongation.

#### The Interaction of Fabricating and Heat Treating Variables

The heat-treating procedures used for Stainless W present no new problems; the methods used for the regular grades of stainless steel apply. Cleaning prior to any heat treatment is necessary to prevent contamination. Although thin sections should be heat treated in a vacuum or under an inert gas, most parts can be heat treated in air. Scale removal can be by either chemical or mechanical methods. Vapor blasting effectively removes annealing scales, while the tarnish developed on aging can be removed either by blasting or by polishing with emery. Pickling, first in a hot sulfuric acid solution and next in a hot solution of nitric and hydrofluoric acids, is also an effective scale-removing procedure. Light scales, such as the tarnish formed on aging, can be removed in a very short time by immersion in the hot nitric-hydrofluoric acid solution alone.

Stainless W may be welded by any of the methods used for the regular grades of stainless steels. Welding operations may be performed on material in the solution annealed, aged, or overaged conditions. If joint efficiencies in excess of 90 per cent in aged material are desired, however, the structure must be solution annealed and aged subsequent to welding.

Billets may be forged after soaking at 2200 F to 2300 F. The soaking time should be sufficient to allow the center of the billet to reach and remain at the forging temperature for a short time. The normal precautions taken when heating stainless steels apply to Stainless W. Cold, thick sections should not be charged into a furnace at the forging temperature, since this may cause internal cracking. Thick sections should be preheated at 1200 F to 1400 F and allowed to equalize at this temperature before they are charged into a hot furnace. Overheating should be avoided since this favors the formation of delta ferrite. Because the reversion of this phase to austenite at normal annealing temperatures is rather sluggish, delta ferrite, if formed, may be retained in the final product. Delta ferrite promotes cracking during hot working. In addition, it may be the cause of anisotropy in wrought products. It does not contribute to the strength of the material.

The machining characteristics of Stainless W in the solution-annealed condition are reported to be better than those of the soft austenitic stainless steels. The material is not gummy and the chips break up. Aged material, although much harder, can also be machined.

#### 17-4 PH

Armco 17-4 PH is supplied in the form of bar, wire, plate, castings, and forging billets. Bar, plate, and wire are usually supplied in the solution heat-treated condition, i. e., annealed at 1900 F and cooled to room temperature. This treatment results in a low-carbon martensite upon cooling to room temperature, the hardness being Rockwell C 30 to 35. Machining operations can be performed without great difficulty on material in this condition. Welding operations are usually made on solution heat-treated material.

Forging billets and forging bars are normally supplied in an overaged condition that is developed by holding solution heat-treated material at 1150 F. This treatment results in a hardness of Rockwell C 30 and places the material in the most suitable condition for sawing. Bar and wire are also supplied in the overaged condition.

Material in the solution-heat-treated condition may be precipitation hardened directly after fabrication. Overaged material must be solution heat treated again prior to precipitation hardening. Holding at 900 F for 1 hour is the recommended aging treatment.

A diagram of heat treatments for 17-4 PH is presented in Figure 8.



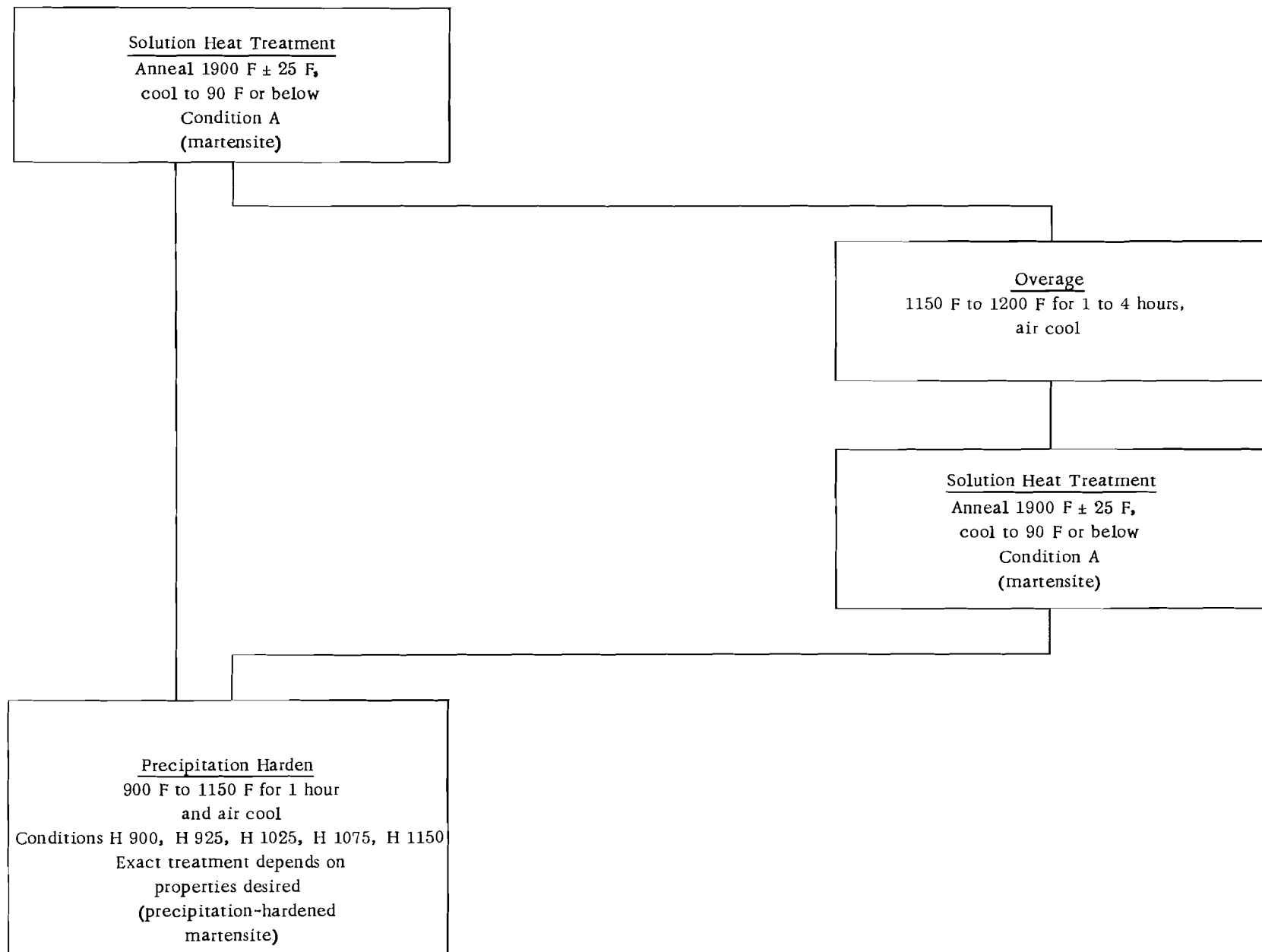


FIGURE 8. THE HEAT TREATMENT OF 17-4 PH

## Heat Treatment

17-4 PH is solution heat treated at  $1900\text{ F} \pm 25\text{ F}$  for 30 minutes to develop what is known as "Condition A". The solution heat treatment takes the element involved in precipitation hardening, copper, into solution. Some carbides remain undissolved, however, since the compounds of columbium and tantalum with carbon are quite stable. In addition, islands of delta ferrite may remain since the proportion of austenite-promoting elements to ferrite-promoting elements is not strongly in favor of austenite.

Upon cooling from the solution heat-treating temperature, 17-4 PH begins to transform from austenite to martensite at about  $270\text{ F}$ . The transformation is essentially complete at  $90\text{ F}$ . The martensite which forms, however, is of very low carbon content and thus is not very strong. Some typical mechanical properties of 17-4 PH in Condition A are presented below.

<u>Property</u>	<u>17-4 PH in Condition A</u>
Ultimate Tensile Strength, psi	150,000
0.20 Per Cent Offset Yield Strength, psi	110,000
Elongation, per cent in 2 inches	12
Rockwell C Hardness	30-35

The martensite formed in 17-4 PH on cooling from the solution anneal is highly supersaturated with copper. The strengthening mechanism comes into play later when this element is allowed to precipitate within the martensite in a controlled fashion. The recommended aging treatment for 17-4 PH is holding 1 hour at  $900\text{ F}$ . This treatment produces the condition known as "H 900". Depending upon the properties desired, however, treatments for 1 to 4 hours at temperatures between  $900\text{ F}$  and  $1150\text{ F}$  may be used. Higher temperatures, or longer treatment times, result in reduced strength and increased ductility. Some typical mechanical properties of material in Conditions H 900 and H 1150 are presented below.

<u>Property</u>	<u>17-4 PH</u>	
	<u>Condition H 900</u>	<u>Condition H 1150</u>
Ultimate Tensile Strength, psi	195,000	145,000
0.20 Per Cent Offset Yield Strength, psi	180,000	125,000
Elongation, per cent in 2 inches	13	19
Rockwell C Hardness	43	33

The nature of the phase or phases precipitating in the temperature range  $900\text{ F}$  to  $1150\text{ F}$  is unknown. There is X-ray evidence that precipitation does take place. The amount of the precipitate is so slight, however, that it cannot be identified by X-ray techniques. It has been speculated that the precipitate is similar to the epsilon phase of the iron-copper system.

Forging billets and blooms, particularly in large sizes, are supplied in an overaged condition similar to Condition H 1150. This material is most amenable to sawing. Before overaged material can be hardened, however, it must be given another solution treatment at 1900 F to redissolve the precipitates.

### The Effects of Variations in Heat Treatment

The recommended solution heat treatment for 17-4 PH is 1900 F  $\pm$  25 F for 30 minutes. Treatment at lower temperatures results in somewhat reduced yield and tensile strengths in Condition H 900 because (1) not quite as much carbon is taken into solution so the martensite formed subsequently is not quite as strong and (2) not quite as much of the precipitating materials is homogeneously dissolved. On the other hand, treating at temperatures above 1900 F causes an increase in the tensile strength and reduction in the yield strength of material subsequently precipitation hardened. Greater solution of carbon at higher temperatures results in a slightly more stable austenite and therefore slightly less transformation on cooling. This accounts for the reduced yield strength. During tension testing, however, the mechanical deformation which takes place after the yield load has been exceeded induces the retained austenite to transform to martensite. This martensite is formed from austenite of somewhat higher carbon content; therefore it is slightly stronger. This accounts for the increased tensile strength. These variations in properties, however, are not very large.

The effects of variations in the duration and temperature of aging treatments have been discussed in a preceding section. For 1-hour treatments the strength of 17-4 PH reaches its peak value between 850 F and 875 F. Measures of ductility, however, reach minimum values in this range of hardening temperatures. The recommended treatment, 900 F  $\pm$  10 F for 1 hour, results in somewhat better ductility at a small sacrifice in strength. Temperatures higher than 900 F result in greater ductility and lower strength as overaging progresses.

### The Interaction of Fabricating and Heat Treating Variables

The 17-4 PH steel may be cut by the procedures commonly used for standard chromium-nickel stainless steels. Cold sawing is recommended over abrasive-wheel cutting. The latter method may induce cracking. Torch cutting, by processes suited to stainless steel, can be accomplished.

The heating of thick sections to the forging temperature, 2150 F, or the annealing temperature, 1900 F, requires certain precautions. Charging thick sections into too hot a furnace may result in internal cracking because

of the high internal tensile stresses developed. The limits listed below should be observed.

<u>Billet Thickness, inches</u>	<u>Maximum Furnace Temperature at Time of Charging, F</u>
Under 4	2150
4-6	2000
6-8	1800
8-10	1600
10-12	1400
12 and larger	1200

If it is necessary to reheat during forging, the steel should be charged into a hot furnace and allowed to heat to 2150 F. A period of 30 minutes for each inch of billet thickness should be allowed for the center of the billet to reach temperature. Billets 3 inches or larger should soak 1 hour at temperature before reworking. Smaller billets should be soaked for a minimum of 15 minutes. Uniformity of temperature throughout the section promotes uniformity of mechanical properties and, thereby, reduces the possibility of cracking during forging.

Cooling after forging should be controlled. Armco recommends that sections thicker than 3 inches, and intricate smaller sections, be returned to the heating furnace and equalized at the forging temperature prior to cooling. Temperature equalization reduces the chances of cracking during cooling. Sections under 6 inches may be air cooled; larger sections should be cooled under a cover of light-gage steel sheet.

Cooling after annealing, likewise, should be controlled. Sections 1/2 inch and under may be water quenched or oil quenched. Bar 3 inches and under should be oil quenched. Sections of 3 to 6 inches should be air cooled, while sections 6 inches or greater should be cooled under cover. Cooling should continue to 90 F or below before hardening to assure complete transformation. Slow cooling of thick sections is necessary to combat cracking which might otherwise occur due to the mechanical strains imposed by the expansion which accompanies the formation of martensite from austenite.

Armco 17-4 PH may be machined either as annealed or as hardened. Excellent finishes can be obtained. The 0.0005 inch per inch contraction which occurs after machining during the final aging treatment can usually be ignored. If tolerances are very close, however, this contraction can be compensated during final machining, since the extent of the contraction is a known function of aging temperature<sup>(27)</sup>. The light tarnish which forms during aging is usually not objectionable.

Wrought 17-4 PH can be welded by many of the arc or resistance welding processes used on standard grades of austenitic stainless steel. Because 17-4 PH cools to a low-carbon, low-hardness martensite, very severe strains are not usually developed when weld joints are cooled. Therefore, no preheating is necessary to avoid cracking of welded joints. However, the alloy is not so tough or ductile as the austenitic stainless grades; care must be taken to avoid unnecessary notch effects. Where high joint strength is sought through post-weld heat treatment 17-4 PH filler metal should be used. Otherwise, a tough austenitic stainless steel, such as AISI Type 308, may be used.

Some difficulty has been encountered with underbead cracking in welding cast 17-4 PH<sup>(28)</sup>. This problem was found to be related to heterogeneity of the copper distribution, a condition eliminated by hot working in wrought material. Restricting copper content to 3 per cent in cast structures has proved very beneficial.

Upon cooling, 17-4 PH weld-metal deposits act similarly to the base metal, starting to transform to martensite at about 270 F. Unless several passes are made no appreciable precipitation occurs in adjacent metal. Full joint strength may be obtained by a post-weld aging treatment alone. When several welding passes are made the successive heating and cooling produces nonuniform strains. In this case, a solution heat treatment prior to hardening permits uniform response and essentially full hardening in the weld zone. Joint efficiencies of 75 per cent can be obtained if the weld metal is not precipitation hardened.

Armco 17-4 PH can be brazed successfully. For best results the flow temperature of the brazing alloy should coincide with the solution heat-treating temperature, so that brazing and annealing may be carried out during a single heating. Controlled atmospheres, or a vacuum, are used to prevent oxidation during this treatment.

## SEMI-AUSTENITIC PRECIPITATION-HARDENABLE STAINLESS STEELS

The semiaustenitic precipitation-hardenable stainless steels have achieved popularity because of a unique combination of properties. As annealed at temperatures near 1950 F, these steels are soft and ductile, having retained their austenitic structure upon cooling to room temperature. In this condition they may be fabricated almost as if they were true austenitic stainless steels. Once fabricated, a series of thermal treatments serves to harden them to high strength levels by causing their austenitic matrix to transform to martensite and by causing precipitation from the martensite. Strength, fabricability, and corrosion resistance are combined in a single material.

The semiaustenitic precipitation-hardenable stainless steels offer yield strengths in the neighborhood of 200,000 psi; they retain a usable proportion of their room-temperature strength at temperatures up to about 900 F. The limiting temperature depends on the alloy, the application, and the duration of exposure at the elevated temperature. These steels are used largely by the aircraft industry for such applications as structures, honeycomb, skins, tanks, ducts, and springs. Nonmilitary products made from these alloys include handsaws, garbage disposal units, valve diaphragms, boat shafts, compressor disks, and nuclear reactor components.

Armco Steel Corporation developed two semiaustenitic precipitation-hardenable stainless steels, 17-7 PH and a newer modification, PH 15-7 Mo. Armco is the sole producer of these materials. Allegheny Ludlum Steel Corporation also developed two semiaustenitic precipitation-hardenable stainless steels, AM 350, and a newer modification, AM 355. Both Allegheny Ludlum and Universal Cyclops produce these materials. The chemical compositions of these four alloys are presented below.

Element	17-7 PH	PH 15-7 Mo	AM 350	AM 355
Carbon, %	0.09 max	0.09 max	0.12 max	0.15 max
Manganese, %	1.00 max	1.00 max	0.90	0.95
Phosphorus, %	0.04 max	0.04 max	0.04 max	0.04 max
Sulfur, %	0.04 max	0.04 max	0.03 max	0.03 max
Silicon, %	1.00 max	1.00 max	0.50 max	0.50 max
Nickel, %	6.50-7.75	6.50-7.75	4.0-5.0	4.0-5.0
Chromium, %	16.00-18.00	14.00-16.00	16.00-17.00	15.00-16.00
Molybdenum, %	--	2.00-3.00	2.5-3.25	2.5-3.25
Aluminum, %	0.75-1.50	0.75-1.50	--	--
Nitrogen, %	--	--	0.07-0.13	0.07-0.13
Iron	Balance	Balance	Balance	Balance

A part of the chromium content of 17-7 PH is replaced by molybdenum in PH 15-7 Mo, a modification which enhances elevated-temperature strength.

The reduced chromium content and increased carbon content of AM 355, by comparison with AM 350, result in greater strength through the elimination of delta ferrite.

The transformation characteristics, and therefore the mechanical properties, of the semiaustenitic stainless steels are very sensitive to composition. For example, the total variation of just chromium and nickel in the above specifications for 17-7 PH and PH 15-7 Mo corresponds to a variation in the  $M_s$  temperature of about 270 F. Since a variation in  $M_s$  of this amount could not be tolerated, the semiaustenitic stainless steels are normally melted to very much closer specifications than those indicated above. Improvements in melting control have reduced the variations in properties among different heats of the same alloy to an extent sufficient for the great majority of applications. For very critical applications, however, some fabricators prefer to run pilot heat treatments on each lot of material received.

#### 17-7 PH and PH 15-7 Mo

Armco 17-7 PH and PH 15-7 Mo are principally sheet and strip products, although other forms are also available. These materials are usually supplied in Condition A, which designates a solution heat treatment at 1950 F. In this condition the alloys are soft and formable, being primarily austenitic. The austenite is stable enough that it does not transform during winter shipment, but it does undergo transformation during deformation. Most fabricating operations are performed on material in Condition A.

Subsequent to fabrication, 17-7 PH and PH 15-7 Mo may be hardened by either of two methods, both of which involve the precipitation of carbides to adjust the austenite stability. A treatment at 1400 F adjusts  $M_s$  and  $M_f$  so that the material is martensitic on cooling to room temperature. A treatment at 1750 F adjusts  $M_s$  and  $M_f$  so that material is austenitic at room temperature but may be transformed by cooling to -100 F. The transformation to martensite results in partial hardening of the matrix. Elements which were soluble in the austenite become trapped in the martensite during the transformation to produce a supersaturated martensitic solid solution. Full strength is developed by allowing the solute elements to precipitate in a controlled fashion.

Mechanical deformation, as well as thermal treatments, is capable of inducing the transformation of austenite to martensite. Sheet material is supplied either as solution heat treated or as transformed by cold rolling. Precipitation from material transformed by cold rolling results in strengths greater than those which can be obtained from thermally transformed material.

A diagram of heat treatments for 17-7 PH and PH 15-7 Mo is presented in Figure 9. Although both alloys are heat treated alike, PH 15-7 Mo, by virtue of its molybdenum content, resists the metallurgical changes which take place at elevated temperatures to a greater extent than does 17-7 PH. In certain applications, PH 15-7 Mo will perform satisfactorily at temperatures 100 F higher than the limiting temperatures for 17-7 PH.

### The Solution Heat Treatment

17-7 PH and PH 15-7 Mo are solution heat treated at 1950 F to develop Condition A. During this treatment carbon and the precipitation-hardening elements are taken into solution. Delta ferrite, in amounts between 5 and 20 per cent, is present in the austenite matrix. Material in Condition A can be fabricated by the procedures used for ordinary austenitic stainless steels. During deformation, however, 17-7 PH and PH 15-7 Mo transform to martensite quite rapidly, necessitating the use of more frequent anneals. Solution heat treatment at 1950 F restores work-hardened material to the soft, ductile condition. Some typical mechanical properties of 17-7 PH and PH 15-7 Mo in Condition A are presented below.

Property	Condition A	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	130,000	130,000
0.20 Per Cent Offset Yield Strength, psi	40,000	55,000
Elongation, per cent in 2 inches	35	35

### Heat Treatment to Obtain Condition TH 1050

Subsequent to fabrication, the austenitic matrix may be transformed to martensite by conditioning at 1400 F for 90 minutes and cooling to 60 F within 1 hour. During the 1400 F treatment, chromium carbides precipitate at the grain boundaries or in other regions of high energy such as slip planes. Intermetallic compounds may also precipitate during the 1400 F treatment, but this has yet to be proved or disproved. The precipitation, by reducing the carbon and alloy content of the austenite, raises  $M_s$ . Upon cooling, austenite begins to transform to martensite at about 200 F. The reaction goes essentially to completion if the cooling from 200 F to 60 F takes place within 1 hour. Slower cooling allows a partial stabilization of the austenite in the presence of its degeneration product, martensite.

The 1400 F treatment, followed by the cool to 60 F, produces Condition T. Some typical mechanical properties of 17-7 PH and PH 15-7 Mo in Condition T are presented on page 38.



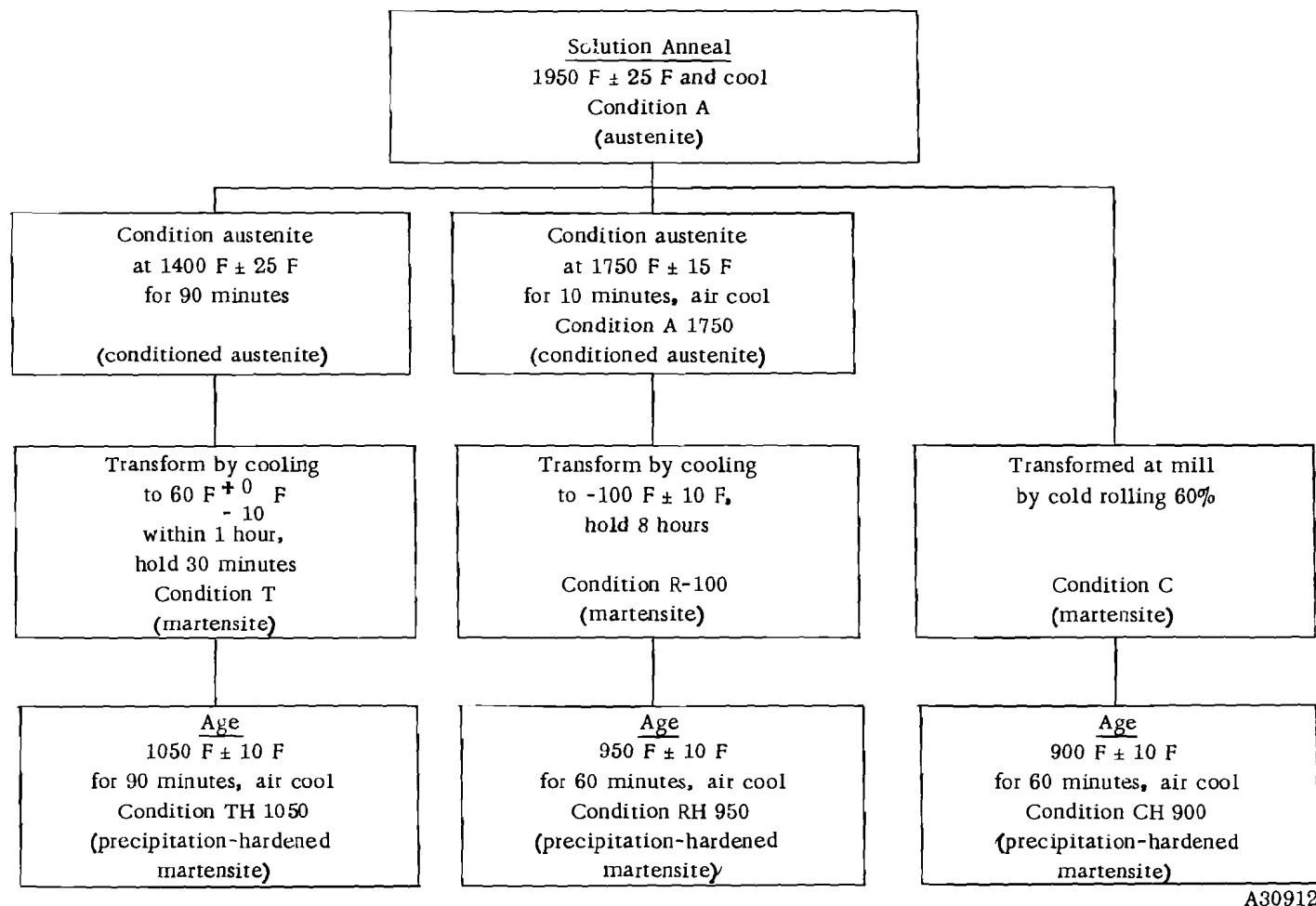


FIGURE 9. THE HEAT TREATMENT OF 17-7 PH AND PH 15-7 Mo

Property	Condition T	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	145,000	145,000
0.20 Per Cent Offset Yield Strength, psi	100,000	90,000
Elongation, per cent in 2 inches	9	7

After the austenite conditioning treatment at 1400 F, about 0.03 per cent carbon remains in solution. Thus, the martensite formed on cooling is not very strong. An aging treatment at 1050 F for 90 minutes, however, produces an additional strengthening effect. During this treatment, a compound believed to be composed of aluminum and nickel, is formed. X-ray analysis indicates the presence of a compound, but so little is present that it cannot be identified. As previously explained, it is the coherent precipitation of this compound which produces the strengthening effect. This aging treatment results in Condition TH 1050. Some typical properties of material in Condition TH 1050 are presented below.

Property	Condition TH 1050	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	200,000	210,000
0.20 Per Cent Offset Yield Strength, psi	185,000	200,000
Elongation, per cent in 2 inches	9	7

#### Heat Treatment to Obtain Condition RH 950

The strengthening technique involving the 1400 F austenite conditioning treatment was the first to be used on 17-7 PH and PH 15-7 Mo and is still the most widely used on these products. Another series of thermal treatments, introduced in 1956, results in somewhat higher strength. In this series of treatments austenite is conditioned at 1750 F for 10 minutes and then air cooled. About 0.04 to 0.05 per cent carbon remains dissolved after this treatment, the remainder having been precipitated in the form of chromium carbide particles. The  $M_s$  is about 60 F after this treatment. On cooling to room temperature the structure remains austenitic.

The 1750 F treatment produces Condition A 1750. Some typical mechanical properties of 17-7 PH and PH 15-7 Mo in Condition A 1750 are presented below.

Property	Condition A 1750	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	133,000	150,000
0.20 Per Cent Offset Yield Strength, psi	42,000	55,000
Elongation, per cent in 2 inches	19	12

Since conditioning at 1750 F results in an  $M_s$  just below room temperature, a subzero treatment is necessary to transform the austenite to

martensite. Refrigeration at -100 F for 8 hours results in virtually complete transformation. Material having received this treatment is designated by Condition R-100. Some typical properties of material in Condition R-100 are presented below.

Property	Condition R-100	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	175,000	180,000
0.20 Per Cent Offset Yield Strength, psi	115,000	125,000
Elongation, per cent in 2 inches	9	7

It will be noticed that the strength of material in condition R-100 is somewhat greater than that of material in Condition T. The strength differential is due to the slightly higher carbon content of the martensite in Condition R-100.

After refrigeration, the aging treatment recommended by the producer is 950 F for 60 minutes. This produces Condition RH 950. The formation of an aluminum-nickel compound within the martensite is thought to be responsible for the hardening observed, just as in the case of the 1050 F treatment used to obtain Condition TH 1050. Some typical properties of material in Condition RH 950 are presented below.

Property	Condition RH 950	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	235,000	240,000
0.20 Per Cent Offset Yield Strength, psi	220,000	225,000
Elongation, per cent in 2 inches	6	6

Material in Condition RH 950 is stronger than material in Condition TH 1050. The strength differential is largely due to the difference in the aging treatments. If material in Conditions T and R-100 were given the same aging treatments, the strength differential would be reduced considerably. The higher carbon content of the martensite in material given the refrigeration treatment, however, would probably account for any remaining strength difference.

#### Heat Treatment to Obtain Condition CH 900

One series of thermal and mechanical treatments is designed to provide maximum strength but limited fabricability. Material annealed at 1950 F is cold rolled 60 per cent prior to shipment. The cold work transforms the austenitic matrix to martensite and results in Condition C. Some typical properties of material in Condition C are presented on the following page.

Property	Condition C	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	220,000	220,000
0.20 Per Cent Offset Yield Strength, psi	190,000	190,000
Elongation, per cent in 2 inches	5	5

Because of its high strength and low elongation, only very mild forming operations may be performed on material in Condition C. Applications include springs and valve diaphragms.

After fabrication, the material is hardened by aging at 900 F for 60 minutes. As in similar treatments to produce Condition TH 1050 and RH 950, the controlled precipitation of an aluminum-nickel compound is thought to produce the observed hardening. The 900 F treatment results in Condition CH 900. Some typical properties of material in Condition CH 900 are presented below.

Property	Condition CH 900	
	17-7 PH	PH 15-7 Mo
Ultimate Tensile Strength, psi	265,000	265,000
0.20 Per Cent Offset Yield Strength, psi	260,000	260,000
Elongation, per cent in 2 inches	2	2

Transformation induced by cold work results in higher strength than does transformation induced thermally. The reason for this is that cold work introduces strain energy as well as inducing transformation. Precipitation from the martensitic matrix results in a sizable additional strength increase, even though the matrix is already strained to a high strength level.

### The Effects of Variations in Heat Treatments

The heat treatments described in the preceding sections are those which, according to tests made by the producer, result in the optimum combination of properties. Variations in these heat treatments naturally affect the properties obtained. Sometimes the recommended procedures may be altered to obtain somewhat different properties. For example, material conditioned at 1400 F is sometimes aged at temperatures between 1080 F and 1120 F rather than at 1050 F to improve ductility, although this results in a reduction of strength. It is useful to know what changes in properties may be expected if variations in heat treatments are made, and why these changes occur.

If during fabrication it becomes necessary to reanneal, the recommended treatment is at 1950 F  $\pm$  25 F to restore Condition A. Variations in annealing temperature between 1900 F and 2000 F have very little effect on the properties of material in Condition A, since a rather stable austenite is formed at any temperature in this range. Annealing at temperatures below

1900 F or above 2000 F, however, is likely to reduce ductility. A less stable austenite accounts for the lower elongation and increased rate of work hardening of material annealed below 1900 F. The larger amounts of delta ferrite and increased grain size tend to reduce the elongation of material annealed above 2000 F.

Variations in the annealing temperature do, however, affect the properties of material subsequently treated to obtain Conditions TH 1050 or RH 950. If the annealing temperature is increased beyond 2000 F, the strength of subsequently hardened material is reduced. The strength change is thought to reflect a change in the amount of martensite formed during the transformation treatments. According to one theory more strain centers are eliminated as annealing temperature is increased. These strain centers are thought to nucleate martensitic shears at temperatures below  $M_s$ . Excepting mechanical deformation, subsequent treatments are not very effective in producing new strain centers. Thus, higher annealing temperatures result in fewer martensite nuclei, reduced transformation, and consequently reduced strength. Annealing at 1950 F, rather than at lower temperatures, is recommended because the elongation of subsequently hardened material reaches its highest values after the material has been annealed between 1900 F and 2000 F. In addition, this annealing treatment results in austenite with an  $M_s$  well below room temperature, thus assuring retention of good ductility in material that might be cooled to subzero temperatures during shipment or storage.

To reach Condition T, a treatment at  $1400\text{ F} \pm 25\text{ F}$  for 90 minutes is recommended. The purpose of this treatment is to precipitate carbides from the austenitic solid solution. The solubility of carbon in austenite decreases with decreasing temperature between 1200 F and 1600 F. At the same time, however, the diffusivity of carbon in austenite, which controls the rate of precipitation, is reduced. These two factors are thought to combine to produce a maximum amount of precipitated carbides for a fixed holding time at some temperature between 1200 F and 1600 F. A maximum amount of precipitate means maximum carbon depletion of the austenite. This in turn raises the  $M_s$  to its highest point and results in maximum transformation on cooling to room temperature. Maximum transformation is almost synonymous with maximum strength, but the argument is complicated slightly by the fact that the amount of carbon remaining unprecipitated determines the strength of the martensite which does form. The maximum strength for material in Condition TH 1050 is realized if Condition T is obtained by treating at 1300 F for 90 minutes. The 1400 F treatment is recommended in spite of the lower strength obtained, however, because it results in greater elongation.

The longer the holding time at 1400 F the greater the strength of material subsequently treated to produce Condition TH 1050. Longer holding times evidently allow more complete carbide precipitation. The

90-minute holding time was selected because it is long enough to produce uniformity and good strength, yet not so long as to make the treatment expensive in terms of furnace time.

The cooling rate from the 1400 F conditioning treatment is an important variable. The producer recommends cooling to 60 F within 60 minutes. Cooling at slower rates, or not cooling to 60 F, results in partial austenite stabilization and consequently less transformation. It has been found, however, that stabilization does not occur in these alloys, in the absence of martensite. Since martensite does not form above 200 F, stabilization occurs only if the cooling rate between 200 F and 60 F is too low.

If austenite stabilization does occur, it can be overcome by cooling to a temperature below 60 F. Cooling to 0 F or -20 F results in virtually complete transformation even after considerable stabilization. Such a treatment, however, may result in more transformation than would occur on rapid cooling to 60 F. When this is the case, ductility suffers.

If Condition RH 950 is to be developed, the austenite-conditioning treatment recommended is  $1750 \pm 15$  F for 10 minutes. As the temperature of this treatment is increased above 1750 F, the strength of material subsequently hardened to Condition RH 950 begins to decrease rapidly. This is because higher temperatures reduce  $M_s$  to values so low that transformation is not complete upon refrigeration at -100 F. Increasing the conditioning temperature lowers  $M_s$  by dissolving more carbon. Increased time at 1750 F has the same effect as increased temperature, except that the decline of strength with increased holding time is much less rapid.

As refrigeration temperature is decreased to about -75 F the amount of transformation is increased. Cooling below -75 F results in very little additional transformation. The amount of transformation increases with longer refrigeration times. Martensite apparently forms both athermally and isothermally in 17-7 PH and PH 15-7 Mo. The recommended refrigeration treatment is  $-100 \text{ F} \pm 10 \text{ F}$  for 8 hours. Minus 100 F is chosen rather than -75 F because refrigeration near -75 F results in minimum elongation. An 8-hour treatment, rather than a shorter treatment, is chosen so that the isothermal component of transformation may more closely approach completion and provide greater consistency of properties.

The effects of variations in the time and temperature of aging treatments have been discussed in a previous section. In Condition TH 1050, 17-7 PH is considerably overaged. Maximum tensile strength is obtained after treating material in Condition T at about 900 F, if the time of treatment is 90 minutes. Such a treatment, however, results in minimum ductility. Greater ductility but somewhat reduced strength is obtained by using the recommended heat treatment,  $1050 \text{ F} \pm 10 \text{ F}$  for 90 minutes. If elongations greater than the typical 9 per cent are required, the temperature

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of the aging treatment may be raised above 1050 F. This, of course, results in a further strength reduction.

In Condition RH 950, 17-7 PH is slightly overaged and PH 15-7 Mo is slightly underaged, i.e., aged at a temperature slightly lower than that which produces maximum strength. The recommended procedure for aging is 950 F  $\pm$  10 F for 60 minutes.

Material in Condition C is more highly strained than material in Conditions T or R-100. For this reason, aging can be accomplished at a slightly lower temperature. The energy required to allow atoms to move into positions where they can form coherent precipitates is supplied by the lattice strain energy and by thermal energy. The more highly strained the lattice, the less thermal energy need be supplied to allow precipitation, i.e., a lower-temperature aging treatment may be used. The recommended precipitation-hardening treatment for material in Condition C is 900 F  $\pm$  10 F for 60 minutes.

#### A Comparison of Conditions TH 1050, RH 950, and CH 900

The strength of 17-7 PH and PH 15-7 Mo is highest in Condition CH 900. Fabricability, however, is quite limited in the material as cold worked. Ductility in the fully hardened condition, likewise, is rather low. If maximum fabricability is needed, the treatments leading to Condition TH 1050 or RH 950 must be chosen.

Material in Condition RH 950 is stronger than material in Condition TH 1050. Material in the latter condition, however, is more ductile. Depending on which property, strength or ductility, is more important in a given application, one series of treatments or the other will be chosen. There is no observable difference in distortion or scaling during heat treatment. Likewise, both series of treatments lead to similar corrosion-resistance properties.

More experience has been gained with the treatments leading to Condition TH 1050 than with the treatments leading to Condition RH 950. This, perhaps, accounts for the greater use of the older heat-treating practice today. The cost of installing refrigeration apparatus may also be a factor.

The properties of material in Condition RH 950 are somewhat more reproducible than those of material in Condition TH 1050. Normal variations in composition between heats of either 17-7 PH or PH 15-7 Mo cause the small corresponding variations in transformation characteristics. After conditioning at 1400 F, cooling to 50 F to 60 F is sufficient to cause virtually complete transformation in most heats. Cooling below 50 F will

assure more complete transformation in some heats but may result in reduced ductility in others. Cooling to 0 F, or below, leads to virtually complete transformation in all heats in spite of normal compositional variations. On the other hand refrigeration at -100 F, after austenite conditioning at 1750 F, leads to essentially complete transformation in all heats. Ductility loss in this case is avoided by refrigerating below -75 F.

Another factor contributes to the difference in reproducibility of properties between material treated to produce Condition TH 1050 and that treated to produce Condition RH 950. At 1050 F the change in properties resulting from a given variation in aging temperature is greater than at 950 F. In engineering terms, the aging curve is flatter at 950 F than at 1050 F. For example, a 20 F increase in aging temperature at 1050 F results in a reduction in tensile strength of about 7000 psi, whereas a 20 F increase in aging temperature at 950 F results in a reduction in tensile strength of only about 2500 psi.

#### The Interaction of Fabricating and Heat-Treating Variables

It is essential that surfaces be cleaned thoroughly before 17-7 PH and PH 15-7 Mo are heat treated. If lubricants are not removed they may cause carburization at elevated temperatures. A change in carbon content can greatly alter response to heat treatment. In addition, sulfur-bearing cutting oils may break down at heat-treating temperatures and allow sulfur penetration. Clean surfaces promote uniform oxidation during thermal treatments and make scale removal much easier.

Cleaning is usually a two-step process. The first step is the removal of lubricants, often by vapor degreasing. The second step is the removal of any remaining dirt, which otherwise might catalyze carbon penetration. This step usually involves mechanical agitation with some agent such as magnesia, followed by a rinse.

Air is the most satisfactory furnace atmosphere for heat treating 17-7 PH and PH 15-7 Mo. At temperatures up to about 1200 F the surface oxidation produces a tarnish, the extent of discoloration increasing with longer times and higher temperatures. At temperatures above 1200 F scaling occurs. The depth of the scale is also a function of time and temperature. The tarnish or scale can be removed either mechanically or chemically.

If surfaces must be kept free of tarnish or scale, heat treatments should be carried out in vacuum. It is difficult to remove water vapor from hydrogen to the extent necessary for scale-free heat treatment in this atmosphere, but acceptable surfaces have been made in this way. Other reducing atmospheres introduce the hazard of carburization or decarburization.



and also result in a very adherent scale. Nitriding may result from the use of dissociated ammonia or nitrogen atmospheres. Furnace brazing, which requires freedom from scaling, is carried out successfully under argon.

Electric furnaces, both of the convection and radiation types, feature good temperature control. Gas- or oil-fired furnaces are less satisfactory from this viewpoint and introduce the possibility of flame impingement. Salt-bath furnaces have been used successfully for heat treatments at temperatures below 1200 F. Carburization and surface penetration, however, can occur during higher temperature heat treatments in baths of presently available commercial salts.

Both tarnish and scale may be removed either mechanically or chemically. Vapor-blasting processes are highly satisfactory mechanical scale-removal methods. They are widely used on 17-7 PH and PH 15-7 Mo. Mechanical scale removal results in material with a higher endurance limit and better corrosion resistance.

The acid pickling methods used for the standard grades of stainless steels may also be used for 17-7 PH and PH 15-7 Mo. As previously explained, however, austenite conditioning sensitizes this material to rapid intergranular attack in acid solutions. Therefore, material which has received an austenite conditioning treatment, at either 1750 F or 1400 F, should not be subjected to acid scale removal. Chemical scale-removal methods may be used on solution-heat-treated material and on material in Condition CH 900. Precipitated carbides are not present in material in either condition. Hydrogen embrittlement does not occur in the soft, austenitic matrix developed by solution annealing. The very light tarnish developed on aging to produce condition CH 900 can be removed by immersion for a very short time in a nitric-hydrofluoric acid pickle. The duration of this treatment is short enough that hydrogen embrittlement does not occur in material in Condition CH 900.

Several scale-softening methods are in use. Among these are immersion in hot sodium hydride, a caustic permanganate solution, or sulfuric acid. The Hooker Electrochemical Company and the Kolene Corporation produce other scale-softening solutions. Scale softening is followed by scale removal, usually by immersion in a 10 per cent nitric acid, 2 per cent hydrofluoric acid solution kept at 110 F to 140 F. If the scale is light the softening step may be omitted.

Operations such as blanking, punching, perforating, shearing, sawing, and cutting by torch or abrasive wheel are usually performed on material in Condition A. The soft austenitic condition is most amenable to these cutting operations.

Forming operations are almost always on material in Condition A. In this condition the material possesses its maximum ductility and minimum

yield strength. If the material work hardens too much before a forming operation is complete, an anneal at 1950 F restores it to the soft austenitic condition.

The increase in energy provided by cold working lowers the temperatures at which nucleation and growth reactions take place. Thus, a part deformed nonuniformly during its fabrication will respond nonuniformly to the 1400 F austenite conditioning treatment. If the deformation produced during fabrication is severe and nonuniform it is recommended that an anneal at 1950 F precede the 1400 F treatment in order to equalize and reduce the residual stresses.

After fabrication, heat treatments at 1400 F or 1750 F will produce some distortion. The distortion may be removed by restriking and holding in the original forming dies while the material is still austenitic. Material in Condition A 1750 may be given this treatment after cooling because it is austenitic at room temperature. Material which is to be treated to Condition T should be restruck during cooling between 1400 F and 200 F, since transformation to martensite begins at about 200 F and is virtually complete at room temperature.

Dimensional changes occur during heat treatment. The austenite-to-martensite transformation is accompanied by an expansion of about 0.0045 inch/inch due to the change in crystallographic structure. Precipitation hardening results in a contraction of about 0.0005 inch/inch due to a slight reversion of martensite to austenite and to the precipitation itself. These factors, as well as scale formation during heat treatment, must be considered in the design of some fabricating operations. Machining to close tolerances is not done on material in Condition A. Scaling during subsequent austenite conditioning at 1750 F or at 1400 F, together with the attendant dimensional changes, would make such an operation impractical. Machining to close tolerances is usually performed on material in Conditions T or R-100. Material in these conditions is harder than material in Condition A, but not so hard as precipitation-hardened material. It can be machined without difficulty at slow speeds. The slight dimensional change upon precipitation hardening can be compensated, or even ignored in some cases. Heating to temperatures up to about 1120 F produces only a light tarnish, which is usually not objectionable.

Some fabricating operations must be performed on fully hardened material. Piercing and dimpling for rivets is an example. If rivet holes are pierced prior to final hardening, the 0.0005 inch/inch contraction which occurs on aging causes a slight misalignment of the rivet holes of the finished piece. Although this contraction is slight, when applied to a 29,000,000 psi modulus of elasticity, stresses of about 15,000 psi could result if a cover plate, for example, were riveted to a rigid frame through holes aligned prior to final heat treatment. 17-7 PH and PH 15-7 Mo can be pierced and dimpled in Conditions TH 1050 and RH 950.

In some instances it is desirable to form material in Condition A 1750. Although the material work hardens very rapidly, mild forming operations may be performed without difficulty. Greater deformation results in higher strength but lower elongation on subsequent hardening, possibly because more complete transformation may result from the straining.

Armco 17-7 PH can be welded by many of the arc and resistance processes used for stainless steels. Care must be taken to avoid loss of aluminum by oxidation at high temperatures, however, since this is the element responsible for the high mechanical properties. The inert-gas-shielded arc-welding processes are well suited to the welding of 17-7 PH because the aluminum in the alloy is then shielded from contact with the air. Filler metal of 17-7 PH is used if high strength through subsequent heat treatment is sought. A tough austenitic stainless steel filler metal may be used if high strength at the weld need not be developed.

The material usually is welded when in Condition A. Since both the welded zone and the base metal remain austenitic upon cooling, thermally induced strains are absorbable. In addition, the delta ferrite formed at welding temperatures combats hot cracking.

The best procedure for hardening after welding includes an anneal at 1950 F prior to the austenite-conditioning and precipitation-hardening treatments. Such a treatment is said to result in joint efficiencies of 94 to 100 per cent with good joint ductility. If the 1950 F treatment after welding is omitted, joint ductility suffers slightly. If material is to be hardened by the series of treatments involving refrigeration, however, a 1950 F anneal after welding and before austenite conditioning at 1750 F, is unnecessary. Elevated-temperature treatments, either at 1950 F or 1750 F, result in enough stress equalization and solution of precipitated phases to improve the ductility of the weld joint.

Overaging, as previously explained, improves ductility at the expense of strength. Since welded areas may be subject to reduced ductility, Armco recommends an aging temperature 25 F higher than otherwise for welded parts.

The material may be resistance spot welded in any condition without much variation in joint strength. In general, however, spot welds are made on transformed or fully hardened material.

Armco 17-7 PH is usually brazed while in Condition A, then transformed by austenite conditioning and cooling and finally precipitation hardened. Sandwich structures are brazed and heat treated in a single operation. The details of sandwich construction have been reported recently<sup>(29)</sup>.

An assembled sandwich structure, with sheets of the brazing alloy in position, is placed between cover plates and graphite slabs in an envelope which is purged and filled with argon. The assembly is then placed in a retort and heated to the brazing temperature, 1650 F to 1725 F for a 92.5 per cent silver, 7 per cent copper, plus lithium brazing alloy. Next the assembly is cooled to 1400 F and held at this temperature for 90 minutes. Cooling to -20 F is followed by precipitation hardening.

The brazing operation must be carried out in argon, helium, or in a vacuum, to avoid oxidation of surfaces during the brazing cycle. Hydrogen atmospheres cannot be used because hydrogen reacts with the graphite slabs.

During cooling from the brazing temperature, a large mass of material remains in contact with the sandwich assembly. For this reason cooling is slow, and carbide precipitation cannot be prevented. Thus, a true Condition A 1750, which requires rapid cooling after austenite conditioning, would be difficult to develop. Therefore, transformation is effected by conditioning at 1400 F and cooling. A few additional carbides may be precipitated during cooling from 1400 F. Slow cooling between the  $M_s$  and  $M_f$ , however, may allow partial austenite stabilization to occur. Subsequent cooling to -20 F overcomes the tendency toward stabilization and assures virtually complete transformation.

The procedure outlined in the preceding paragraphs is currently being used in commercial production of 17-7 PH sandwich-construction panels. For PH 15-7 Mo, however, a different thermal cycle is now being tested by numerous aircraft companies. The assembly is placed in a retort, heated to the brazing temperature (1650 F to 1725 F), and held at temperature for 10 to 20 minutes. The assembly is then cooled as rapidly as possible to 1000 F. This may take from several minutes to a few hours, depending upon equipment and panel size. Subsequently, the panel, still held in fixtures to maintain flatness, is refrigerated at -100 F for 8 hours. Final aging is done at 950 F. The tooling, brazing alloy, and atmospheres are the same as those used for 17-7 PH.

#### AM 350 and AM 355

AM 350 was placed on the market by Allegheny Ludlum in December, 1954, as a bar, plate, sheet, and strip product. This alloy, containing 15 to 20 per cent delta ferrite as annealed, could not be hardened uniformly in thick sections because chemical segregation resulted in nonuniform distribution of delta ferrite. AM 355, with less chromium and more carbon, was developed and placed on the market in 1955. This alloy can be hardened uniformly in thick sections because it contains no delta ferrite. Subsequently, the segregation problem in AM 350 was removed when consumable-electrode vacuum-arc melting was introduced. AM 350, however, has

remained primarily a sheet and strip product. AM 355, because of its slightly better mechanical properties, is supplied in sheet form as well as in the form of bar and plate.

AM 350 and AM 355 sheet products are usually supplied as H-annealed, in which condition they are soft, austenitic, and not susceptible to martensite transformation during shipment. Hardening, subsequent to fabrication, is achieved through heat treatment. One series of treatments involves the precipitation of carbides at 1710 F to adjust the  $M_s$  to about 100 F. The other series of treatments involves carbide precipitation at 1375 F (with a prior 1710 F treatment optional) to adjust the  $M_s$  to about 375 F. Transformation of austenite to martensite takes place on cooling to -100 F in the former case and on cooling to room temperature in the latter case. Transformation after the 1710 F treatment can also be effected by mild deformation, such as by stretching 10 per cent. Subsequent to transformation, further increases in strength are brought about by tempering at 850 F. Modifications of these heat treatments are used for bar and plate products.

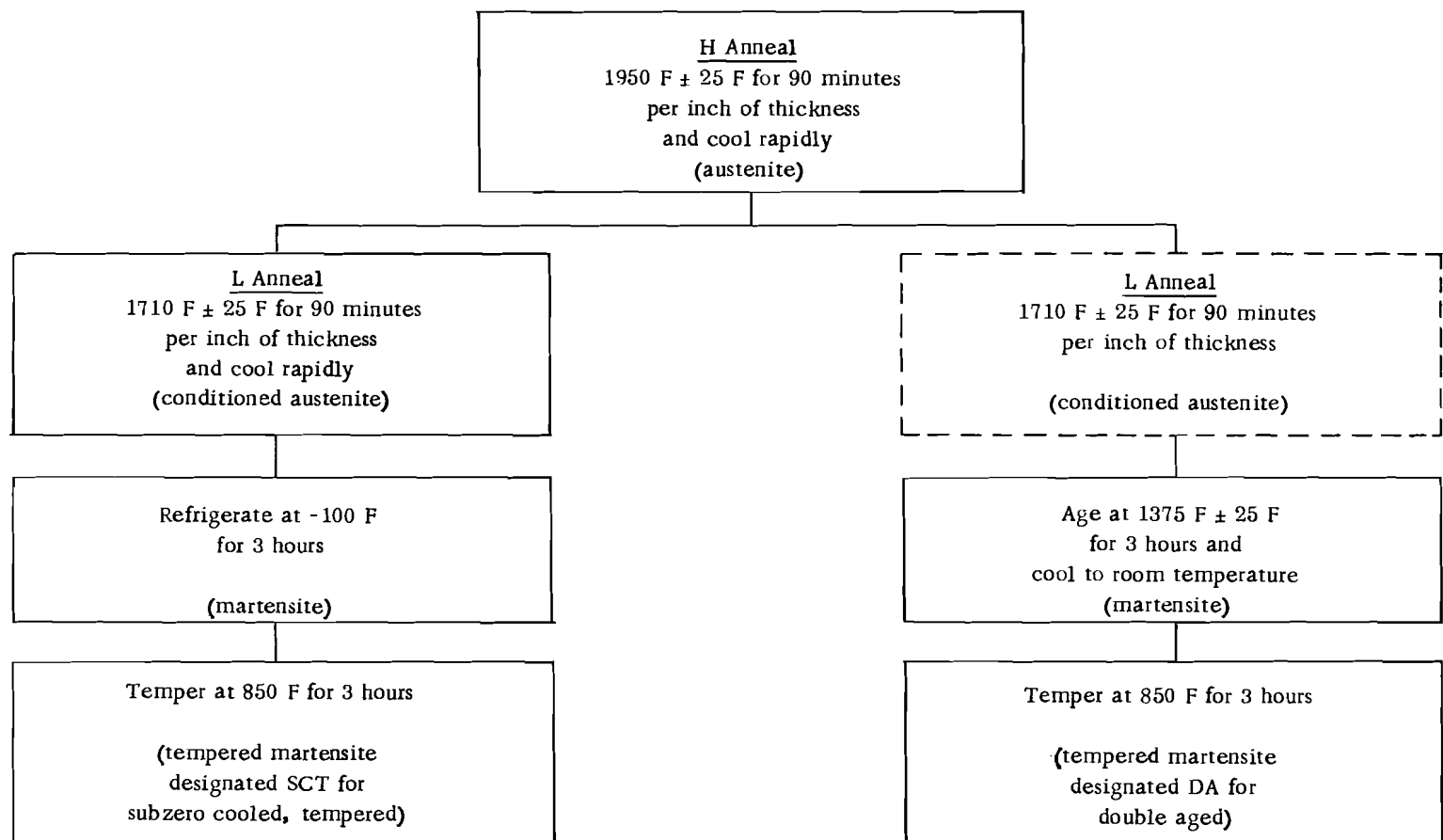
Figures 10, 11, and 12 are diagrams of the standard heat treatments performed on AM 350 and AM 355.

### The H-Anneal

The H-anneal is a high-temperature solution anneal that imparts maximum formability to sheet products. Bar products are not H-annealed because they are usually not subjected to severe cold-forming operations. During the H-anneal, carbon is taken into solution by the austenite matrix, adjusting the  $M_s$  to a temperature below -100 F. Thus, austenite is retained on cooling to room temperature.

In AM 350, the balance of austenite-promoting and ferrite-promoting elements is such that 15 to 20 per cent of the microstructure of H-annealed material is made up of delta ferrite. However, AM 355, which contains more carbon and less chromium than AM 350, is virtually free of delta ferrite. This difference in microstructure is the primary factor accounting for the differences in the heat treatment of the two alloys. AM 350 is H-annealed at 1950 F, whereas AM 355 is H-annealed at 1875 F. The delta ferrite in AM 350 restricts grain growth at elevated temperatures and thereby allows a higher annealing temperature to be used for this alloy.

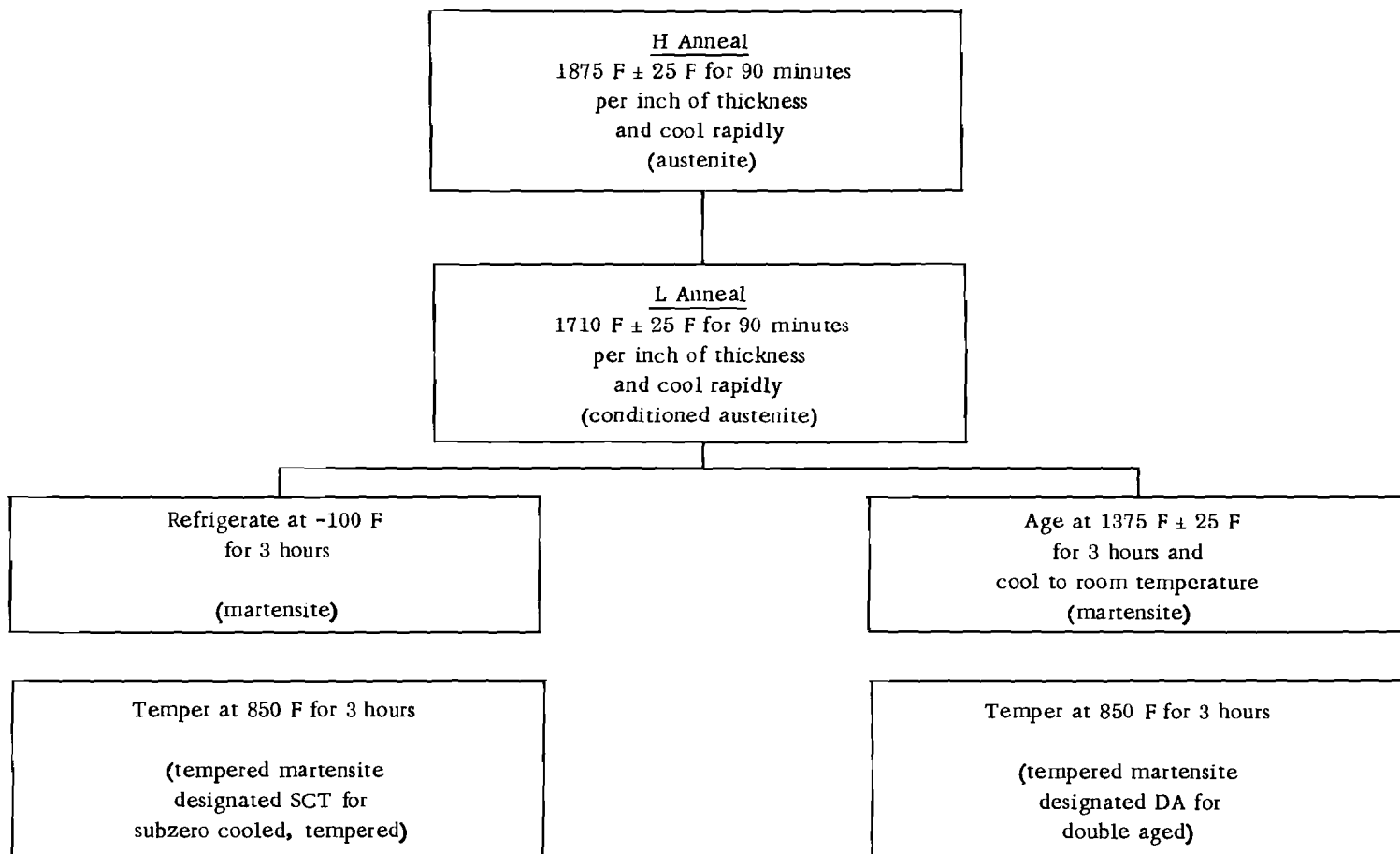
The austenite formed during the H anneal is soft and ductile. It can be cut, formed, and welded by the procedures used for the regular austenitic stainless steels. One characteristic of the austenite of these semi-austenitic alloys is that it is somewhat less stable than that of the austenitic stainless steels. As a result, during cold working AM 350 and AM 355 work harden more rapidly than do the austenitic steels because more austenite transforms to martensite. Under severe forming operations



\*Optional treatment.

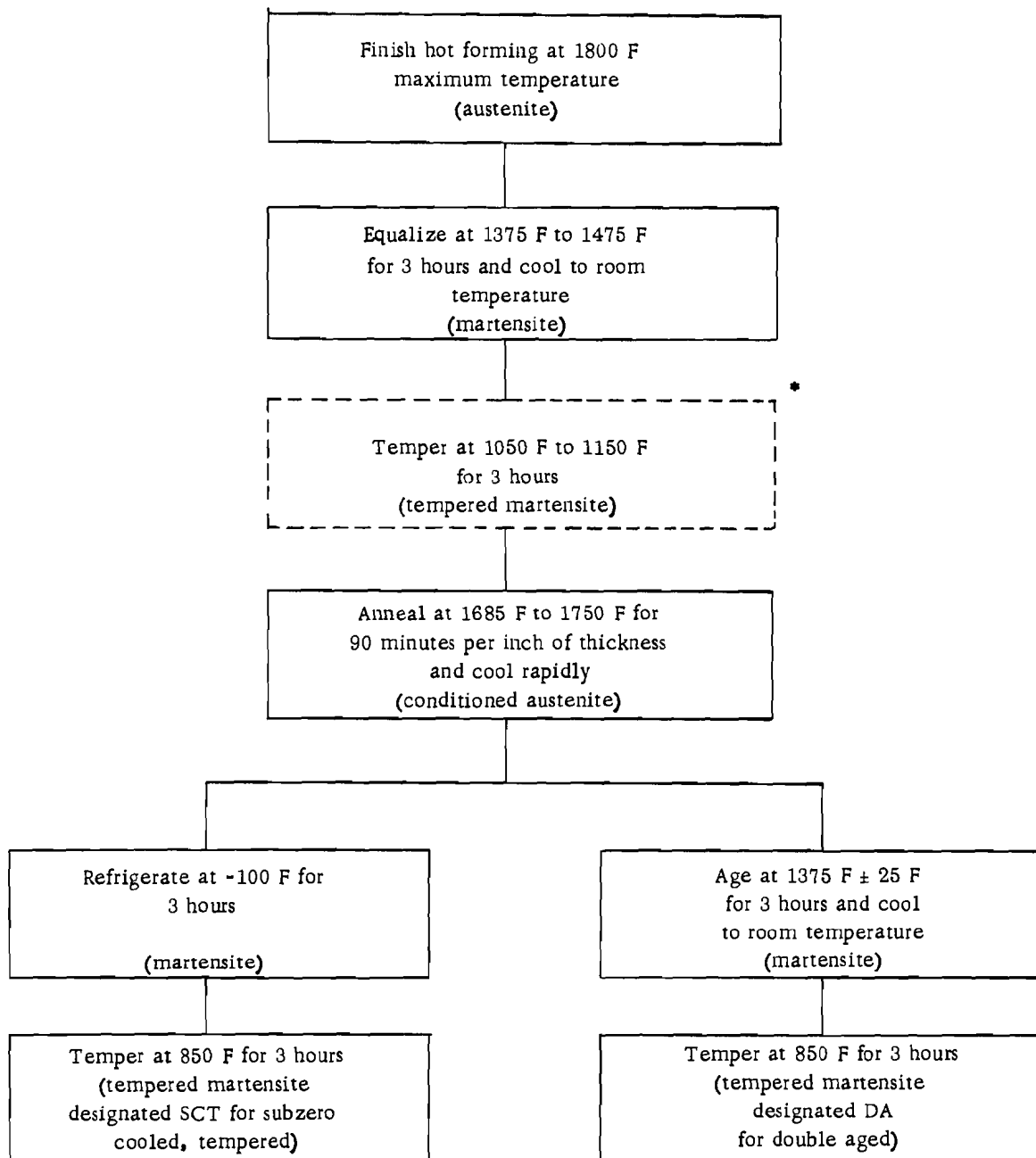
A30913

FIGURE 10. THE HEAT TREATMENT OF AM 350 SHEET



A30914

FIGURE 11. THE HEAT TREATMENT OF AM 355 SHEET



\*Optional treatment.

A30915

FIGURE 12. THE HEAT TREATMENT OF AM 355 BAR



an intermediate anneal may be necessary to restore ductility. The H-anneal procedure is used in this case.

Some average mechanical properties of H-annealed material are presented below for illustrative purposes.

Property	H-Annealed	
	AM 350	AM 355
Ultimate Tensile Strength, psi	149,000	187,000
0.20 Per Cent Offset Yield Strength, psi	63,000	56,000
Elongation, per cent in 2 inches	39	28.5

### SCT Treatments

If austenite is to be transformed to martensite by subzero cooling, the range of transformation temperatures must first be adjusted so that complete transformation can be obtained. This is accomplished by L-annealing, i.e., holding for a short time at 1710 F. During this treatment about 0.05 to 0.06 per cent carbon is retained in solution, while the remainder precipitates in the form of chromium carbide,  $\text{Cr}_{23}\text{C}_6$ . The precipitate particles form primarily at the austenite-delta ferrite interfaces in AM 350 and at the grain boundaries in AM 355. In material cold worked subsequent to the H-anneal, precipitation of carbides during the austenite-conditioning treatment may also occur within the austenite grains along the traces of active slip planes. The reduction in the carbon and chromium content of the austenite results in an increase in  $M_s$  from below -100 F to a value just above room temperature and an increase in  $M_f$  to about -100 F. Thus, on cooling from the L-anneal the structure consists primarily of austenite, but also contains precipitated carbides, a small amount of martensite, and delta ferrite in the case of AM 350.

Some illustrative mechanical properties of L-annealed material are presented below.

Property	L-Annealed	
	AM 350	AM 355
Ultimate Tensile Strength, psi	166,000	195,000
0.20 Per Cent Offset Yield Strength, psi	56,000	60,000
Elongation, per cent in 2 inches	20	15

While the L-anneal adjusts the carbon content of the austenite to a reproducible level, normal variations in the other elements of the composition result in a variation in  $M_s$  in different heats of the same alloy. The mechanical properties of L-annealed material are sensitive to these variations in  $M_s$ .

Cooling to -100 F and holding at this temperature for 3 hours after L-annealing results in virtually complete transformation of austenite to martensite. AM 355 is almost entirely martensitic after this refrigeration treatment. AM 350, however, is only 70 to 90 per cent martensitic after subzero cooling. The remainder of the microstructure is composed of 5 to 15 per cent delta ferrite and 5 to 15 per cent retained austenite. The latter constituent is uniformly dispersed among the martensite plates. The delta ferrite is not altered during subzero cooling and thus does not contribute to the hardening of AM 350. Because the entire microstructure of AM 355 can be hardened by transformation, this alloy is stronger than AM 350. Some illustrative mechanical properties of material in the subzero cooled condition are presented below.

Property	Subzero Cooled	
	AM 350	AM 355
Ultimate Tensile Strength, psi	200,000	--
0.20 Per Cent Offset Yield Strength, psi	110,000	130,000
Elongation, per cent in 2 inches	12	--

Subsequent to transformation, full strength is developed by tempering the martensite at 850 F for a period of 3 hours. During this treatment the martensitic structure actually becomes stronger without loss of ductility. This behavior, which is characteristic of some martensitic stainless structures, contrasts with the behavior of plain-carbon steels, as explained previously.

Some average mechanical properties of AM 350 and AM 355 as sub-zero cooled and tempered are presented below.

Property	SCT	
	AM 350	AM 355
Ultimate Tensile Strength, psi	201,000	216,000
0.20 Per Cent Offset Yield Strength, psi	172,000	181,000
Elongation, per cent in 2 inches	12.8	11.4

The hardening of AM 350 and AM 355 is primarily due to martensite formation and to the tempering of this martensite. Coherent precipitation of a second phase during the normal 800 F, 3-hour tempering operation is unlikely. Holding for long periods of time in the neighborhood of 800 F, however, results in a hardness increase. This is indicative of true precipitation hardening. The precipitate may be a chromium-rich ferrite.

#### DA Treatments

Austenite can be transformed to martensite on cooling to room temperature, rather than -100 F, if the range of transformation temperatures is adjusted properly. This can be accomplished by conditioning the austenite

for 3 hours at 1375 F. During this treatment the precipitation of chromium carbides depletes the austenite of all but 0.02 to 0.03 per cent carbon. The  $M_s$  temperature is raised to 350 F to 400 F and the  $M_f$  is raised to a level above room temperature. This aging treatment is similar to the L-anneal in its function of raising the transformation range. The aging treatment, however, raises  $M_s$  and  $M_f$  more than does the L-anneal because it results in greater depletion of carbon through chromium carbide precipitation. Martensite forms from austenite on cooling from the 1375 F treatment.

Some typical mechanical properties of AM 350 in the aged condition are presented below.

Property	AM 350 as Aged at 1375 F for 3 Hours
Ultimate Tensile Strength, psi	160,000
0.20 Per Cent Offset Yield Strength, psi	105,000
Elongation, per cent in 2 inches	10

Somewhat better strength properties are obtained in AM 350 if the 1375 F aging treatment is preceded by an L-anneal at 1710 F. The dual treatment, 1710 F followed by 1375 F, results in more uniform and perhaps more complete, carbide precipitation. While the dual treatment is optional in the case of AM 350, it is quite advantageous in the case of AM 355. The newer alloy, lacking delta ferrite, has fewer sites for carbide precipitation. Martensite forms on cooling to room temperature after the second austenite conditioning treatment, i.e., the 1375 F aging treatment.

As in the case of material transformed by subzero cooling, the full strength of material treated at 1375 F, or at 1710 F and 1375 F, is developed by tempering at 850 F for 3 hours. Some typical mechanical properties of material L-annealed at 1710 F, aged at 1375 F, and tempered at 850 F (double aged) are presented below.

Property	DA	
	AM 350	AM 355
Ultimate Tensile Strength, psi	195,000	195,000
0.20 Per Cent Offset Yield Strength, psi	155,000	155,000
Elongation, per cent in 2 inches	10.5	10

Double-aged material is not as strong as subzero-cooled and tempered material. This can be traced to the difference in the carbon content of the martensite formed in each case. The carbon content of the martensite in double-aged material is only 0.02 to 0.03 per cent, whereas subzero cooled and tempered material is composed of martensite with 0.05 to 0.06 per cent carbon. The difference in mechanical properties would be

greater if it were not for the nitrogen trapped in the martensite. This element has the same effect as carbon in hardening martensite, but nitrogen is not precipitated like carbon during the treatments at 1710 F or 1375 F.

### CRT and SCCRT Treatments

Two processing methods, which involve cold rolling in amounts up to 35 per cent in conjunction with thermal treatments, have recently been applied to AM 350 and AM 355. The condition designated CRT is developed by cold rolling, to produce transformation, followed by tempering. The condition designated SCCRT is developed by subzero cooling and cold rolling, to produce transformation, followed by tempering. In either case material is supplied by Allegheny Ludlum in the fully hardened condition, making it unnecessary for the consumer to perform any heat treatments. AM 355 sheet material is available at several strength levels as illustrated below.

Property	AM 355				
	CRT				SCCRT
Ultimate Tensile Strength, psi	210,000	230,000	245,000	350,000	290,000
0.20 Per Cent Offset Yield Strength, psi	180,000	210,000	240,000	335,000	280,000
Elongation, per cent in 2 inches	20	16	8	1	2

The exact details of the treatments leading to the conditions designated CRT and SCCRT, as well as the metallurgical changes which accompany these treatments, are regarded as proprietary information by Allegheny Ludlum.

### The Effects of Variations in Heat Treatments

Because AM 350 and AM 355 work harden rapidly because of martensite formation, severe forming operations may necessitate the use of intermediate anneals. Good formability in AM 350 is restored by H-annealing at 1950 F  $\pm$  25 F and cooling rapidly to produce austenite. Higher annealing temperatures result in increased amounts of delta ferrite and larger grain size, both of which may be detrimental to the properties of hardened material. Delta ferrite, which is retained during subsequent heat treatments, does not contribute to the hardening of the alloy. The larger the grain size the less uniform will be the precipitation of carbides during treatments at either 1710 F or 1375 F. Reduced strength and corrosion resistance may result. H-anneal temperatures much lower than 1950 F result in a less homogeneous distribution of carbon in the microstructure and less stress relief. As previously explained, this results in a less stable austenite at room temperature, and consequently reduced formability.

To restore formability to work-hardened AM 355 material, it is H-annealed at  $1875\text{ F} \pm 25\text{ F}$  and cooled rapidly. This treatment allows the martensite formed during working to revert to the soft austenite. The lower temperature is used in the case of the newer alloy since no delta ferrite is present to restrict grain growth. Somewhat lower ductility results from the reduced H-anneal temperature.

Final anneals should be at  $1710\text{ F} \pm 25\text{ F}$  followed by rapid cooling. Higher temperatures result in a depressed  $M_s$  because they allow more carbon to remain in solution; subsequent cooling to  $-100\text{ F}$  may not bring about complete transformation. Temperatures much lower than  $1710\text{ F}$  result in greater carbide precipitation and higher  $M_s$  temperatures. While complete transformation can be obtained on cooling to  $-100\text{ F}$ , the martensite formed is lower in carbon content and, consequently, not as strong.

The recommended refrigeration treatment is  $-100\text{ F}$  for 3 hours. Holding at either higher or lower temperatures has been observed to result in reduced hardness. Temperatures above  $-100\text{ F}$  possibly result in reduced amounts of athermally formed martensite, while temperatures below  $-100\text{ F}$  possibly result in a reduction in the amount of isothermally formed martensite. Longer holding times at  $-100\text{ F}$  result in somewhat increased strength and reduced elongation, effects which are indicative of more complete transformation. The recommended 3-hour holding time represents a compromise between the strength and ductility obtained on subsequent tempering. The effects of time and temperature on the subzero martensitic transformation are not well understood in terms of fundamental reactions.

Aging at  $1375\text{ F}$  for 3 hours results in maximum carbide precipitation and therefore maximum  $M_s$  and  $M_f$ . Higher aging temperatures result in less complete transformation because more carbon is soluble in austenite at these higher temperatures. Lower aging temperatures likewise result in less complete transformation. Although somewhat less carbon is soluble at lower temperatures, complete precipitation of carbides is hampered by a lower diffusion rate. When aged as recommended, the  $M_f$  temperatures of AM 350 and AM 355 are sufficiently high that cooling to room temperature results in virtually complete transformation. The  $1375\text{ F}$  - 3-hour aging treatment appears to offer the best compromise between properties and aging time. Stabilization of austenite during cooling from  $1375\text{ F}$  is not a problem.

Rapid cooling is specified after treatments at  $1950\text{ F}$ ,  $1875\text{ F}$ , or  $1710\text{ F}$ . The primary function of these treatments is to adjust the level of the carbon dissolved in the austenite. After annealing at  $1950\text{ F}$  or  $1875\text{ F}$  all the carbon is in solution. Slow cooling would allow carbide precipitation, thereby defeating the purpose of these treatments. After annealing at  $1710\text{ F}$  about half of the carbon is in solution, the remainder being in the form of precipitated chromium carbides. Slow cooling might allow additional carbide precipitation and thereby preclude attainment of the desired

transformation characteristics. Precipitation of carbides at temperatures below 1375 F occurs so slowly, however, that the cooling rate after aging is not critical. Only very slow cooling after aging at 1375 F would allow additional carbide precipitation.

The recommended tempering treatment, 3 hours at 850 F, produces maximum hardening. Greater ductility, with a corresponding decrease in strength, may be obtained by tempering at slightly higher temperatures.

#### A Comparison of SCT, DA, CRT, and SCCRT Treatments

About 90 per cent of the AM 350 and AM 355 sheet products sold are treated to produce the SCT condition. Material in this condition has greater strength than double-aged material by virtue of the higher carbon content of its martensite. The corrosion resistance of subzero-cooled and tempered material is higher than that of double-aged material, since the former treatment produces fewer precipitated carbides. The corrosion resistance of AM 355 in the SCT condition compares favorably with that of AISI Type 304.

CRT and SCCRT conditions have the advantage of very high strength. In addition, the consumer does not heat treat these materials since they are supplied in the fully hardened condition. The limited fabricability of ultra-high-strength material in the CRT and SCCRT conditions, however, restricts the range of application.

#### The Interaction of Fabricating and Heat Treating Variables

Before heat treating AM 350 and AM 355 it is essential that surfaces be very clean. Lubricating oils can break down at elevated temperatures and cause contamination or even corrosion. At best, the scale will be difficult to remove if surfaces are not thoroughly cleaned. Heat treating material without first removing previously formed scales will produce a scale that is quite difficult to remove. Time can be saved by removing the scale after each heat treatment.

The cleaning method recommended by Allegheny Ludlum is immersion in an aqueous caustic solution maintained at about 160 F followed by a rinse in the purest possible water. This treatment removes dirt, lubricants, and any products formed by the breakdown of lubricants. An optional treatment is immersion of cleaned work in hot dilute nitric acid to remove the last traces of surface contaminants, again followed by a rinse in the purest possible water. All work should be dry before it is heat treated.

When material has been cleaned properly the heat treating atmosphere is not critical, except in that carburizing or nitriding atmospheres should be avoided. The scale produced on heat treating in air is easily removed. If scale-free heat treatment is necessary, as in the case of furnace-brazing operations, atmospheres of dry hydrogen, helium, or argon, as well as a vacuum, may be employed.

Both mechanical and chemical scale-removal methods are used on AM 350 and AM 355. The standard scale removal method is immersion for 2 to 3 minutes in an aqueous solution of 10 per cent nitric acid and 2 per cent hydrofluoric acid maintained at about 140 F. Variations in this procedure include a prior treatment in a sulfuric acid solution or in molten-salt scale-softening baths in the case of very heavy scales. Material which has been aged at 1375 F is sensitive to intergranular attack in acid solutions. Scale removal from this material should be by some mechanical means, such as vapor blasting. A very brief immersion in the nitric-hydrofluoric acid solution should follow to remove the last traces of scale. The tarnish formed on tempering can usually be removed by a 30-second immersion in the nitric-hydrofluoric acid solution.

Fabricating operations are usually performed on H-annealed material. Forming operations are most easily performed on material in this condition. If the subsequent treatment at 1710 F results in any distortion, corrections can be made before the -100 F treatment since AM 350 and AM 355 are essentially austenitic as L-annealed.

The dimensional changes which occur on transformation and tempering must be considered in the design of forming operations. Both alloys undergo an expansion of about 0.0045 inch/inch on transformation and a contraction of about 0.0004 inch/inch on tempering. Stretch forming material treated at 1710 F in amounts of 10 per cent or more results in nearly complete transformation. Fabricating by stretch forming, therefore, has two advantages: (1) The 0.0045 inch/inch expansion due to martensite formation is absorbed in the forming operation; and (2) the need for the -100 F treatment is removed.

AM 350 and AM 355 may be welded by any of the processes suitable for austenitic stainless steels<sup>(30)</sup>. The inert-gas-shielded arc and resistance welding methods, however, are especially well-suited to these alloys. Material is usually welded in the H-annealed condition, the weld metal being hardened along with the base metal during subsequent thermal treatments. Hardened structures may also be welded, but must be made austenitic, transformed, and tempered subsequently if joint efficiencies of 90 to 100 per cent are to be obtained. An advantage of welding fully hardened material is the reduced over-all dimension change on subsequent rehardening.

If filler metal is needed to make a weld joint, either AM 350 or AM 355 may be used. If full strength need not be developed at the weld,

a tough austenitic stainless steel filler may be used. When a weld joint is to be hardened by double aging it is advantageous to cool below room temperature after the 1375 F treatment. This practice assures complete transformation in the weld zone, an area usually less homogeneous than the base metal. After transformation, the ductility of a welded joint may be adjusted by alteration of the tempering treatment. Higher temperatures result in better elongation but correspondingly reduced strength.

AM 355 bar stock is heat treated somewhat differently than are AM 355 sheet products. Bars are more often machined than formed. Therefore, heat treatments are designed to provide the best machinability rather than the best formability. Rather than being H-annealed, bars are hot worked to size and finished at a maximum of 1800 F to produce a fine-grained structure. Subsequent equalization at 1375 F to 1475 F for 3 hours and cooling to room temperature results in a homogeneous structure of chromium carbides in a low-carbon martensite. Overtempering at 1050 F to 1150 F then produces the structure which is most amenable to machining operations. If machining operations are not planned, of course, the tempering treatment may be omitted. The final hardening treatments are the same for both bar and sheet material. An L-anneal may be followed either by double-aging treatments or by subzero-cooling and tempering treatments. Double-aging treatments, however, are not frequently applied to bar products.



## AUSTENITIC PRECIPITATION-HARDENABLE STAINLESS STEELS

The austenitic precipitation-hardenable stainless steels have been used mainly in applications requiring exposure to temperatures in the range 900 F to 1300 F. These materials retain a large proportion of their room-temperature strength at temperatures in this range. In cooling from the solution-annealing temperature, supersaturation of precipitation-hardening elements is the result of decreasing solid solubility of these elements in austenite. The degree of supersaturation which can be attained in this way is much less than that produced by transformation of austenite to martensite. A lower degree of supersaturation means a smaller driving force for precipitation. Temperatures in the neighborhood of 1300 F are required to produce precipitation from austenitic matrixes, whereas precipitation from martensitic structures usually takes place in the neighborhood of 900 F. Service temperatures up to the hardening temperature do not cause very large reductions in strength. Therefore, the austenitic stainless steels dominate the applications at the higher temperatures. These materials are sometimes classed as high-temperature alloys or superalloys. For applications below about 900 F, however, the martensitic-base steels (martensitic and semiaustenitic steels) provide superior strength.

High strength at temperatures in the range 900 F to 1300 F is required for applications such as compressor blades, turbine disks, and spacer rings. The austenitic precipitation-hardenable stainless steels are also used for structural components and bolting of aircraft frames near the engine.

The austenitic precipitation-hardenable stainless steels remain austenitic during fabrication and during hardening. Thus, they may be fabricated without difficulty. Once fabricated and hardened, items made from these materials are nonmagnetic. This property, together with corrosion resistance and high strength, makes these materials ideal for mine casings, mine-sweeper parts, and certain electromagnetic applications. Furthermore, dimensional changes during hardening are very small, since there is no martensitic transformation involved in this step.

There are several austenitic precipitation-hardenable stainless steels available. A-286, Discaloy, W-545, and J-1300 contain about 15 per cent chromium, 25 per cent nickel, and 2 per cent titanium. They are all modifications of the German alloy, Tinidur. The modifications include the addition of molybdenum and precipitation-hardening elements to act in conjunction with titanium. Two other alloys, HNM and 17-10 P, contain about 18 per cent chromium, 10 per cent nickel, and 0.25 per cent phosphorus. A-286 and HNM are discussed in this report because their physical metallurgy is typical of the two groups of austenitic precipitation-hardenable stainless steels.

A-286 was developed by Allegheny Ludlum Steel Corporation; it is produced by Allegheny and several other steel companies. This alloy has the following percentage chemical composition:

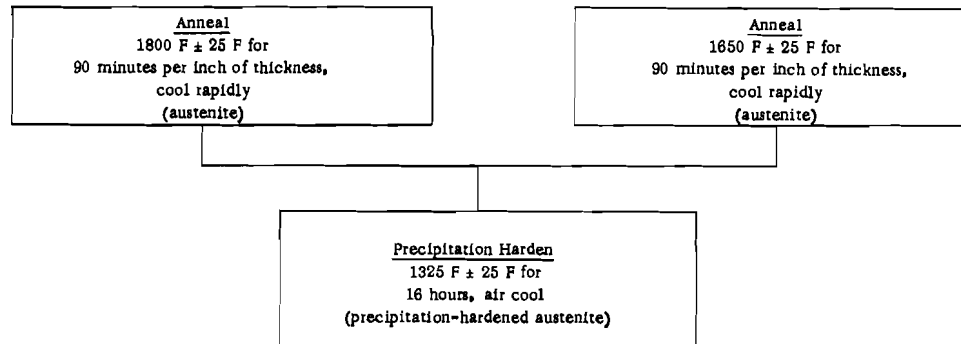
Carbon	0.08 max
Manganese	1.00-2.00
Silicon	0.40-1.00
Sulfur	0.04 max
Phosphorus	0.04 max
Chromium	13.50-16.00
Nickel	24.00-28.00
Molybdenum	1.00-1.50
Titanium	1.50-2.25
Vanadium	0.10-0.50
Aluminum	0.35 max
Iron	Balance

HNM, produced by Crucible Steel Company of America, has this percentage chemical composition:

Carbon	0.30
Manganese	3.50
Phosphorus	0.25
Sulfur	0.04 max
Silicon	0.50
Chromium	18.50
Nickel	9.50
Iron	Balance

#### A-286

Allegheny Ludlum Steel Corporation produces A-286 exclusively by the consumable-electrode, vacuum-arc-melting process. This process results in improved cleanliness, a lack of segregation, and better mechanical properties. The alloy is available in the form of forgings, billets, bars, sheet, strip, foil, tubing, and wire. Material is available in several conditions but is most often supplied in the solution-heat-treated condition. Fabricating operations are performed on material in this condition, after which the material is hardened by aging at 1325 F. An outline of heat treatments is presented in Figure 13.



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FIGURE 13. HEAT TREATMENT OF A-286

### Heat Treatment

A-286 is solution annealed at either 1800 F or at 1650 F. In either case austenite is present at these temperatures and is retained on cooling. Titanium carbides are present in the microstructure. The 1800 F anneal produces a larger grain size. The elements taken into solution during annealing are retained in solution by rapid cooling. These elements are less soluble at room temperature than at elevated temperatures, however, and the austenite becomes supersaturated with them on cooling. Typical mechanical properties of A-286 as solution annealed at 1800 F are presented below.

<u>Property</u>	<u>A-286 as Solution Annealed at 1800 F</u>
Ultimate Tensile Strength, psi	91,000
0.20 Per Cent Offset Yield Strength, psi	37,000
Elongation, per cent in 2.25 inches	47.5

Subsequent to solution annealing, A-286 is precipitation hardened at 1325 F for 16 hours. During this treatment the compound  $\text{Ni}_3(\text{Al}, \text{Ti})$  is formed coherently with the austenitic matrix. Some typical mechanical properties of precipitation hardened A-286 are presented below.

<u>Property</u>	<u>A-286 as Precipitation Hardened</u>
Ultimate Tensile Strength, psi	146,000
0.20 Per Cent Offset Yield Strength, psi	100,000
Elongation, per cent in 2.25 inches	25

Selection of the solution-annealing temperature depends on the properties desired in hardened material. The lower anneal temperature, 1650 F, results in better room-temperature strength, higher ductility, and improved fatigue strength. The 1800 F anneal results in better creep and rupture strengths. Still better creep and rupture strengths may be obtained by annealing at 2050 F prior to aging, but ductility is reduced by this treatment.

#### The Interaction of Fabricating and Heat Treating Variables

The cleaning, heat treating, and scale-removal procedures used for AM 350 and AM 355 are also recommended for A-286.

During threading operations in the manufacture of bolts, certain areas are cold worked about 2 per cent. During subsequent heat treatments very large grains may develop in these areas. To prevent this, A-286 rod and wire can be ordered as cold drawn about 20 per cent.

Forming operations on A-286 increase the energy available for precipitation, so severely deformed areas precipitate and harden at lower temperatures than do less severely formed areas. To prevent nonuniform response during aging, fabricated items may be reannealed prior to this treatment. Another means of combating nonuniform response is to overage at 1400 F for 16 hours prior to aging at 1300 F for 16 hours. During the 1400 F treatment the areas with the greatest fabricating strains overage first. This treatment tends to equalize the strain energy in the structure so that uniform response may be obtained during the 1300 F hardening treatment. If, on the other hand, deformation during fabrication was uniform the equalization may be omitted and the work aged at a lower temperature. A-286 cold worked about 20 per cent, for example, reaches maximum hardness after aging at 1200 F for 16 hours.

A-286 is machined by the procedures used for austenitic stainless steels. As solution annealed the material is gummy, so machining is usually done on hardened material. Machinability can be improved by overaging for several hours at 1500 F. After this treatment, however, complete heat treatment is necessary to restore full strength.

Welding operations on relatively thin sections of A-286 are best performed by one of the inert-gas-shielded techniques. Some difficulty is encountered in welding heavy sections. It is thought that a low-melting phase forms at welding temperatures and penetrates the grain boundaries of the base metal adjacent to the weld zone, producing hot shortness. Although rapid cooling after welding combats this effect, welding of sections thicker than 1-1/2 inches is not recommended. Hastelloy W is often used as filler metal in the welding of thick sections. For best mechanical properties the work should be solution annealed and aged subsequent to welding.

HNM

Crucible Steel Company of America produces HNM, the alloy designation standing for "hardenable nonmagnetic". The alloy is available both as air melted and as consumable-electrode, vacuum arc melted. Forms available include sheet, bar, billets, and forgings. Material is usually supplied in the solution-heat-treated and pickled condition. The material is fabricated in this condition and hardened by precipitating carbides at 1350 F. An outline of heat treatments is presented in Figure 14.

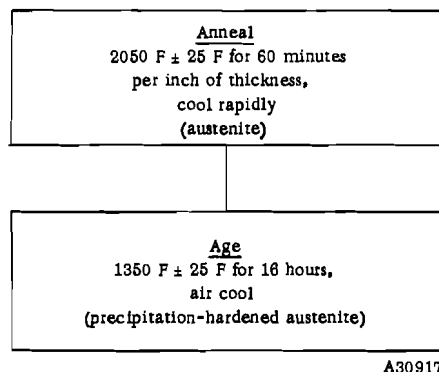


FIGURE 14. HEAT TREATMENT OF HNM

Heat Treatment

HNM is solution annealed at 2050 F. This temperature is just high enough to cause solution of all of the chromium carbide. The use of higher temperatures results in a more uniform distribution of carbon but also causes grain coarsening. This results in greater strength but reduced ductility in subsequently hardened material. In order to retain carbon in solution during cooling, sections thicker than 4 inches should be water quenched. Sections between 5/8 and 4 inches are oil quenched, while thinner sections may be air cooled. Typical mechanical properties of HNM as solution annealed at 2050 F are presented below.

<u>Property</u>	<u>HNM as Solution Annealed at 2050 F</u>
Ultimate Tensile Strength, psi	116,000
0.20 Per Cent Offset Yield Strength, psi	56,000
Elongation, per cent in 1.4 inches	57.5

Subsequent to fabrication, HNM is hardened by aging at 1350 F for 16 hours. Normally such a treatment would produce carbide precipitation only at the grain boundaries. Interstitially dissolved phosphorus, however, seems to increase lattice strain to the extent that sites for carbide precipitation are produced within the austenite grains<sup>(31)</sup>. Therefore, carbides precipitate within the austenite grains, as well as at the grain boundaries. While there is no evidence to indicate that the carbides form coherently with the matrix, they have a hardening effect since they represent a uniform dispersion of fine, hard particles in a soft matrix. Some typical mechanical properties of HNM in the aged condition are presented below.

<u>Property</u>	<u>HNM as Aged at 1350 F for 16Hours</u>
Ultimate Tensile Strength, psi	168,000
0.20 Per Cent Offset Yield Strength, psi	124,000
Elongation, per cent in 1.4 inches	19.5

Aging at temperatures above 1350 F results in better ductility and improved impact strength, but reduced hardness. Aging at temperatures slightly lower than 1350 F may result in higher hardness, but the treatment may have to be extended beyond 16 hours. Maximum hardness is reached at 1200 F, for example, only after 50 to 100 hours. Higher aging temperatures produce fewer but larger precipitate particles, whereas lower aging temperatures produce many fine precipitate particles, provided time for their formation is available.

#### The Interaction of Fabricating and Heat Treating Variables

The cleaning, heat-treating, and scale-removal procedures applicable to most stainless steels may also be employed in the handling of HNM. Since continuous grain-boundary carbides are not developed during heat treatment, acid pickling may be used as a scale removal method.

Fabricating operations which include mechanical deformation have an effect on the response to aging. The additional lattice strain introduced by deformation accelerates the precipitation of carbides during aging. Uniformly worked items may be aged at temperatures somewhat lower than 1350 F to develop maximum hardness. Items with varying amounts of cold work should be solution heat treated before aging if uniformity is desired.

Machining operations are usually performed on solution-annealed material. Due to scaling during aging, however, final machining must be done on aged material.

Welding is not generally recommended because of the likelihood of hot shortness, a phenomenon attributed to the formation of a low-melting

constituent at welding temperatures. The low-melting constituent is possibly a phosphide, since sheet material of reduced phosphorus content has been welded successfully. Reduction of phosphorus content to less than 0.20 per cent, the highest level at which good welds can be made, however, leads to a loss in the hardness of aged material. The steel can be furnace brazed without difficulty.

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